SYMMETRICAL DI-ISOPROPYL-HYDRAZINE AND RELATED COMPOUNDS

BY

HARRY LOUIS LOCHTE

B. A., University of Texas, 1918

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1922

URBANA, ILLINOIS

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

May 23 1922

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY

SUPERVISION BY HARRY LOUIS LOCHTE

ENTITLED SYMMETRICAL DI-ISOPROPYL-HYDRAZINE AND RELATED COMPOUNDS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

THE DEGREE OF Doctor of Philosophy

W. A. Noyes
In Charge of Thesis

W. A. Noyes
Head of Department

Recommendation concurred in*

Roger Adams
J. H. Reedy
B S Hopkins
E. H. Williams
S. A. Braley

Committee
on
Final Examination*

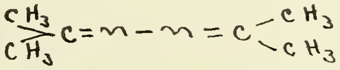
*Required for doctor's degree but not for master's

ACKNOWLEDGEMENT.

The writer wishes to express his appreciation of the inspiration and the helpful suggestions of Professor W.A.Noyes under whose direction this investigation was carried out.

He also wishes to express his gratitude for the never-failing help of Professor J.R.Bailey, of the University of Texas, at whose suggestion this investigation was begun and under whose direction the first part of the work was carried out.

I INTRODUCTION

When reports on the success of catalytic methods of reduction, using platinum or palladium as catalysts and hydrogen gas as reducing agent, showed more and more cases in which complexes could be reduced that had not been reducible before, Professor Bailey, of the University of Texas, suggested the reduction of dimethylketazine,  $(CH_3)_2C=N-N=C(CH_3)_2$, by this method. Although all old methods had failed, catalytic reduction proved comparatively easy. The problem was then transferred to the University of Illinois where the work was continued under the direction of Professor W.A.Noyes.

The preparation and study of various derivatives of the hydrazo compound (symmetrical diisopropylhydrazine) was next undertaken because heretofore aliphatic hydrazines have been too difficult to prepare to study them in detail. The mono-nitroso derivative of symmetrical diisopropyl-hydrazine was prepared and proved very interesting because, contrary to expectations, it forms a sodium salt. The question of the structure of nitroso-hydrazines and their metal salts is thus raised again.

Both the azo and the hydrazone compound corresponding to the symmetrical hydrazine were prepared as the first case of isolation of both tautomers of purely aliphatic compounds of this type.

Primary isopropyl-hydrazine was prepared by reduction of a mixture of equimolecular amounts of acetone, hydrazine-hydrate, and hydrochloric acid; by the acid hydrolysis of acetone-isopropyl-

hydrazine; and by the acid hydrolysis of 2,2'-azobispropane.

II THEORETICAL

Since the discovery of hydrazine by Curtius,[1] and the development of a method, by Raschig[2], by means of which hydrazine and its salts may now readily be made at reasonable cost, the interest in the many types of hydrazines and their derivatives has grown constantly.

Emil Fischer[3] made the first derivative of hydrazine when he prepared and studied, in great detail, the poisonous base, phenyl-hydrazine, made by him through the reduction of diazobenzene. Methods of preparing aromatic hydrazines are quite numerous and these compounds have long been thoroughly studied.

For the aliphatic hydrazines, however, few methods of preparation are known and almost without exception the yields obtained by methods known before the discovery of the method used in this investigation, are poor.

For the preparation of the unsymmetrical secondary hydrazines Emil Fischer [4]worked out a method that gives fair yields. He prepared the nitroso compounds of secondary amines and reduced these with zinc dust and acetic acid. Another method of preparing unsymmetrical hydrazines was developed by the same chemist and may be expressed by the equation[5]:

$C_6H_5\text{-NH-NH}_2 + RBr \longrightarrow C_6H_5(R)\text{N-NH}_2\cdot HBr$. This method is usually used only to prepare mixed disubstituted hydrazines.

[illegible]

[illegible]

[illegible]

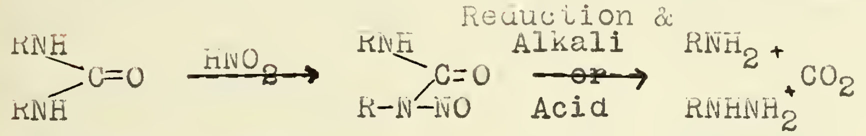
[illegible]

[illegible]

[illegible]

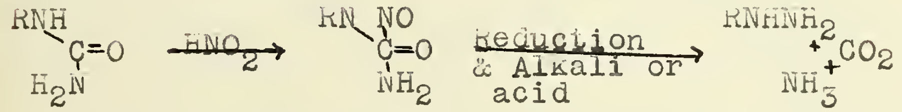
[illegible]

For the preparation of simple primary hydrazines, Fischer [6] also developed a method. It may be illustrated by;



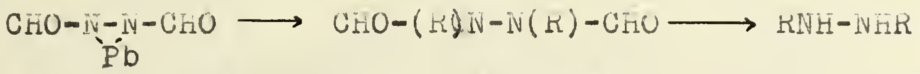
$$\begin{matrix}RNH\\RNH\end{matrix}\!>\!C{=}O \xrightarrow{HNO_2} \begin{matrix}RNH\\R{-}N{-}NO\end{matrix}\!>\!C{=}O \xrightarrow[\text{Acid}]{\text{Reduction \& Alkali } \cancel{\text{or}}} \begin{matrix}RNH_2 +\\ + CO_2\\ RNHNH_2\end{matrix}$$

and by;



$$\begin{matrix}RNH\\ \\ H_2N\end{matrix}\!>\!C{=}O \xrightarrow{HNO_2} \begin{matrix}RN\ NO\\ \diagdown\ \ \\ C{=}O\\ |\\ NH_2\end{matrix} \xrightarrow[\text{\& Alkali or acid}]{\text{Reduction}} \begin{matrix}RNHNH_2\\ + CO_2\\ NH_3 +\end{matrix}$$

For symmetrical disubstituted hydrazines the use of alkyl halides (usually the bromide) yields a mixture of symmetrical and unsymmetrical hydrazines which may usually be separated with more or less difficulty. A more serious difficulty exists through the fact that it is almost impossible to prevent the formation of the quarternary ammonium compounds.[7] The safer and more economical method of preparing these hydrazines by alkylation protects the second H on each nitrogen atom by acetylation or formylation. Then the alkyl groups must go to different nitrogens and thus produce the symmetrical secondary hydrazines. This is the method that was used with some success by Harries and coworkers[8]. They were able to prepare the symmetrical dimethyl and diethyl hydrazines by;

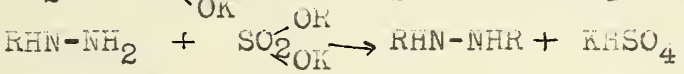


$$\underset{\diagdown Pb \diagup}{CHO{-}N{-}N{-}CHO} \longrightarrow CHO{-}(R)N{-}N(R){-}CHO \longrightarrow RNH{-}NHR$$

The yield was low though and they were able to do little more than isolate the above compounds. Stolle[9] also did much work on this method of preparing aliphatic hydrazines and he and coworkers were able to adjust conditions so as to obtain a certain, if small, yield of symmetrical hydrazines. Busch [9] was able to prepare under these conditions, small quantities of primary isobutylhydrazine and smaller yields of the corresponding symmetrical and unsymmetrical secondary compounds.

Busch and Stolle[9] also used yet a different method for the preparation of symmetrical disubstituted hydrazines. Their method may be expressed by;

$$NH_2NH_2.H_2O + SO_2{<}^{OR}_{OK} \longrightarrow NH_2NHR + KHSO_4 + H_2O$$ and



$$RHN\text{-}NH_2 + SO_2{<}^{OR}_{OK} \longrightarrow RHN\text{-}NHR + KHSO_4$$

Even here the yield is poor and uncertain since sometimes symmetrical and sometimes unsymmetrical hydrazines are formed as the main yield.

Kischner[10] developed a method that was originally used for the preparation of primary hydrazines according to the reactions;

$$RR'CH\text{-}NH_2 + Br_2 + KOH \longrightarrow RR'CH\text{-}NHBr + KBr + H_2O$$

$$RR'CH\text{-}NHBr + RHN\text{-}CHRR' \longrightarrow RR'CH\text{-}NH\text{-}N{=}CRR' + 2HBr$$

The hydrazone thus formed is then hydrolyzed, if the primary hydrazine is to be formed. Catalytic reduction should easily reduce the same hydrazone to the symmetrical secondary hydrazine.

Finally, Curtius and students[11] found that hydrazine hydrate and aldehydes or ketones condense to form simple hydrazones;

$$RR'C{=}O + H_2N\text{-}NH_2.H_2O \longrightarrow RR'C{=}N\text{-}NH_2 + 2\ H_2O.$$

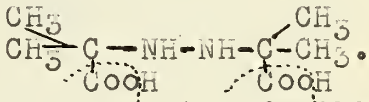
These compounds are very unstable and are either hydrolyzed to the original substances or they react with another mol of aldehyde or ketone to produce azines;

$$RR'C{=}N\text{-}NH_2 + O{=}CRR' \longrightarrow RR'C{=}N\text{-}N{=}CRR' + H_2O$$

Although Curtius and others[12] were able to reduce benzalazine and some other aromatic azines, they found that the aliphatic azines are perfectly stable towards alkaline reducing agents while no

reducing agents could be used in an acid medium because the azines are readily hydrolyzed by acids.

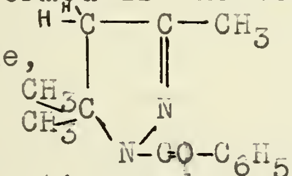
Curtius as well as Wohl and Oesterlin[13] made primary benzylhydrazine by partial reduction of benzalazine and hydrolysis of the hydrazone formed.

Dimethyl-ketazine,on reduction,yields symmetrical diisopropyl-hydrazine and this , in turn, yields azobispropane and other interesting compounds. Always hoping that the reduction could be effected in some way, a number of chemists have recorded failures in attempts to reduce this compound. Curtius[14] tried to reduce the ketazine by alkaline reducing agents, but found it perfectly stable towards these. Thiele[15] could not reduce it by an electrolytic method with which he had just reduced benzalazine to the corresponding hydrazo compound. He also attempted [16] to prepare the symmetrical hydrazine he had hoped to obtain by reduction of dimethyl-ketazine through the elimination of 2 molecules of carbon dioxide from hydrazo-isobutyric-acid,  $(CH_3)_2C(COOH)-NH-NH-C(COOH)(CH_3)_2$. Wieland[17] reports that the aliphatic aldazines are not reducible. Mailhe[18] was able to effect the reduction, but the product obtained consisted of a mixture of mono and di isopropyl-amine instead of the hydrazo compound he sought to obtain.

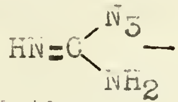
In the course of the present investigation many unsuccessful attempts were made to reduce dimethyl-ketazine by various common reducing agents, acid, neutral, and alkaline. Although a few, such as sodium amalgam(4%), sodium in alcohol, and aluminium amalgam gave small amounts of reduction products that were basic

none of them were identical with the symmetrical hydrazine that was being prepared, in the meantime, by the catalytic method described hereafter. Other reducing agents such as zinc in acid solution, potassium hydroxide and aluminium, iron with hydrochloric acid or acetic acid, and reduction by stannous chloride; all failed to give any noticeable reduction of the ketazine.

In testing for a possible basic product formed during one of the unsuccessful attempts described above, white needles of a different compound separated out on adding benzoyl chloride in the hope of obtaining a benzoyl compound of the reduction product. The melting point, appearance, and analyses indicate that the product formed is the benzoyl derivative of 3-methyl-5-dimethyl-pyrazoline,



Curtius and coworkers, Franke, and Frey and Hoffman[18] found that ketazines, if they have a methyl group next to the C=N complex, readily rearrange, when under the influence of dilute acids to form pyrazolines. Dimethyl-ketazine, thus treated, rearranges to form 3-methyl-5-dimethyl-pyrazoline. Even maleic acid is able to cause this rearrangement in the case of this ketazine. Curtius and Wirsing[19] found that the same pyrazoline is also formed when mesityl oxide is treated with hydrazine. They prepared a benzoyl derivative of the compound thus prepared. The properties given by them agree with those found in the present investigation. The small acid concentration due to hydrolysis and to formation of the derivative is then sufficient to produce this rearrangement of dimethyl-ketazine.

Ziehl[20] attempted the catalytic hydrogenation (Skita method) of a series of compounds of nitrogen. Among these were; iminotriazomethane ——  $HN=C\begin{smallmatrix}N_3\\NH_2\end{smallmatrix}$ — and diazoaminobenzene. He was not able to reduce any of the $N=C$ or $N=N$ complexes shown. In experiments with isocyanides he was able to reduce the compounds to the corresponding methyl-amine derivatives only in case the isocyanides were so stable that no formic acid was formed. In the case of iminotriazomethane he could observe no absorbtion of hydrogen, although he found that camphor oxime could readily be reduced to bornyl- amine.

Quite recently, Staudinger, using a catalytic method of reduction, reduced diazo compounds and obtained hydrazones, but did not reduce these to the hydrazine. In view of the fact that, as will be shown later, salification of the base formed during the reduction is essential to success in the reduction of most such compounds, it is possible that he, too, could have reduced the $C=N$ complex readily if he had run the last step of this reduction in an acid solution.

The work on this problem shows that the reduction of dimethyl ketazine, and probably of other azines, can be carried out with very satisfactory yields through the use of catalytic methods of reduction employing finely divided platinum or palladium either as the platinum or palladium black, or in form of the protected colloid of either metal.

Catalytic reduction by the use of these metals has been known for over half a century, but the possibilities of these methods were not recognized until after the year 1900 and inten-

sive investigation of these methods was not begun until after 1907. Since then three main methods have been worked out; (1) the Willstätter method,[22] using platinum black prepared according to the method of Loew[23];(2)the Paal method[24] employing colloidal platinum or palladium protected by the sodium salt of either protalbinic acid or lysalbinic acid, available only for reduction in alkaline or neutral solutions;(3) the Skita method[25] uses gum arabic instead of the sodium salt of an acid as a protective colloid. In the case of the Skita method the protective colloid is effective in either acid, neutral, or alkaline solution . At the end of the run the colloid is removed by precipitation with acetone and filtering. Skita also originated the principle of inoculation in catalytic reduction[25a]; a small amount of platinic or palladous chloride is reduced separately, by partial reduction in hot alkaline solution by means of a few crystals of hydrazine hydrochloride in case of the platinum, and by passing hydrogen gas through the hot palladous chloride solution, in case of the palladium. A few cubic centimeters of this stock solution is then employed as a "seeding" colloid that aids in the reduction of the main mass of platinum, which,in turn, catalyzes the reduction of the substance in question.

--- **** ----

As it appeared to be the most convenient and the most promising for the reduction of the azines, Skita's method was selected for work at the University of Texas. It was successful from the start although early runs on ketazine, water, and colloidal platinum protected by a small amount of gum arabic, required a large amount of catalyst. Often as much as 100 c.c. of 10% chloroplatinic

acid had to be employed in the reduction of 100 c.c. of dimethylketazine. Even with the large amount of catalyst the yield was only about eighty per cent and several days were required for completion of the reduction. In attempting to improve the yield or at least curtail the amount of platinum, it was found that neutralization of the base formed as the reduction proceeds immensely accelerates the reaction and makes it possible to complete the reduction in a single day with less than one fourth of the amount of platinum formerly used. The extra chloroplatinic acid used in the initial experiments probably owed its main effect to the hydrochloric acid liberated on reduction of the acid, rather than to the additional amount of colloidal platinum this added to the reduction mixture . Since then an article by Skita[25e] has appeared in which he makes the same observation on the effect of hydrochloric acid in a similar case. Experience in this research indicates that salification is always advantageous when a base is formed in catalytic reduction.

During the first few neutralized runs the necessary hydrochloric acid was added at different times during the run because it was feared that hydrolysis of the ketazine by a greater concentration of acid would diminish the yields obtained. Later it was found that, in spite of the claims of Curtius and others that ketazine is immediately hydrolyzed by mineral acids[18],the addition of the theoretical amount of acid at the beginning of the run in no way diminishes the yield of 90-95% of theoretical (based on the amount of ketazine used) which is obtained when the

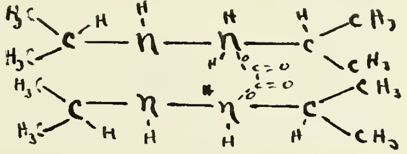
neutralization is done in steps.

Since this unexpected result seems to indicate that dimethylketazine is not hydrolyzed to an appreciable extent by the dilute mineral acid under the conditions of the experiment, it appeared likely that reduction of a mixture of one mol of hydrazine hydrate, one mol of hydrochloric acid, and two mols of acetone would give the same results while, at the same time obviating the isolation, with rather unsatisfactory yields, of the ketazine. In three runs, where in each case, 25 g. of hydrazine hydrate in 250 c.c. of water were employed, the reduction required 3-4 hours and the yields were 78,80,and 74 g. of the hydrochloride of symmetrical diisopropylhydrazine. Although only once recrystallized and therefore not pure, samples of this salt melted at 197-8°, had a chlorine content of 23.8 % (by titration with silver nitrate by Mohr's method), and 3 iodine titrations gave an average purity of 95.3% (2 atoms of iodine to 1 mol of the hydrazine) thus indicating a yield that is practically quantitative.

The hydrazo compound formed in the reduction of dimethyl ketazine is similar, in the main, to other symmetrical hydrazines. As is often the case with aliphatic hydrazines, it is difficult to obtain the base completely anhydrous. Like symmetrical dibenzyl, and in contrast to symmetrical dimethyl and diisobutyl hydrazines which form both neutral and acid salts[27], the base derived from dimethyl ketazine, in all reactions so far observed, is monobasic. The behavior towards mild oxidizing agents iso different from that of the corresponding dimethyl and diethyl compounds.

The preparation of the usual simple salts and derivatives of hydrazines offers no difficulties in the case of the symmetrical hydrazine, except in the case of the benzoyl derivative which does not appear in satisfactory crystalline form but as a smear which could not be made to crystallize. This behavior of the benzoyl derivative is rather common, however, in the case of hydrazo compounds.[28]

Although it is one of the most beautiful and one of the most easily prepared derivatives of symmetrical diisopropyl-hydrazine, the oxalate is troublesome because, as in a number of other oxalates of hydrazo compounds,[29] it seems to form a mixture of salts. In the case of the base under consideration the abnormal results obtained on analyses seem to have been due to the fact that the salt consisted of a mixture, possibly of the simple and the double oxalates. After 6-8 recrystallizations from alcohol the product obtained has a melting point of 200° and analyses show that the compound has the formula;

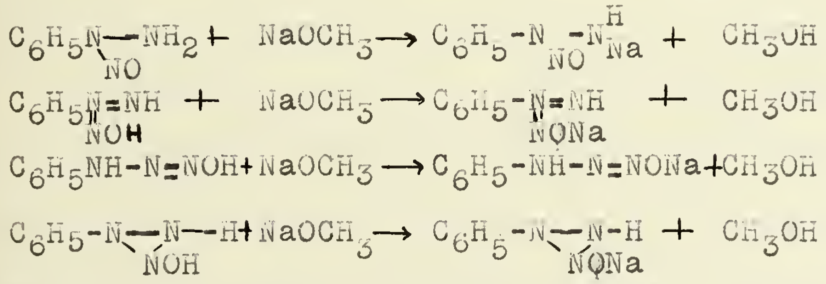


When a mono-alkyl hydrazine is treated with nitrous acid, the imide hydrogen atom is substituted as is seen from the fact that these nitroso-hydrazines still condense with aldehydes. In the presence of amyl nitrite and alkali the nitroso mono-alkyl hydrazines can often be made to react again with nitrous acid[30] to form an isoazotate, $R-N=NONa$.

The mono-aryl-hydrazines here, as in most other respects do not differ greatly from the aliphatic ones. In the case of phenyl-

hydrazine and its substitution products and in the case of benzylhydrazine, sodium salts are formed from the nitroso compounds. This metal may then readily be replaced by alkyls when alkyl halides are permitted to react with the salts. The structure of these sodium salts has not yet been definitely established, probably two or more tautomeric forms exist in equilibrium, somewhat as in the case of acetoacetic ester or in the oximes.

In the case nitrosophenyl-hydrazine a sodium salt is formed when the base is allowed to react with sodium methylate in the absence of water. The sodium replaces an H from phenylhydrazine, but the exact hydrogen atom involved has not yet been definitely determined. The salt could be formed by any one of the following reactions;



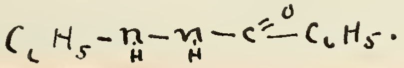
1) $C_6H_5\underset{NO}{N}-NH_2 + NaOCH_3 \longrightarrow C_6H_5-\underset{NO}{N}-N\overset{H}{}Na + CH_3OH$

2) $C_6H_5\underset{NOH}{N}=NH + NaOCH_3 \longrightarrow C_6H_5-\underset{NONa}{N}=NH + CH_3OH$

3) $C_6H_5NH-N=NOH + NaOCH_3 \longrightarrow C_6H_5-NH-N=NONa + CH_3OH$

4) $C_6H_5-\underbrace{N-N}_{NOH}-H + NaOCH_3 \longrightarrow C_6H_5-\underbrace{N-N}_{NONa}-H + CH_3OH$

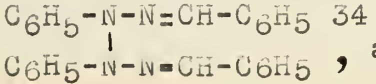
The third form is made extremely unlikely because of the similarity of nitrosophenyl-hydrazine to alkyl nitrosohydrazines, especially nitrosobenzyl-hydrazine, in which the presence of an amino group is established through the condensation of the nitroso-hydrazine with aldehydes.[31] Moreover, careful oxidation of the nitroso compound with cupric salts leads to a hydroxylamine derivative. This compound could hardly form unless the structure were that given in 1) under the conditions of the experiment[32]. Finally, the reduction of the benzoyl derivative of nitrosophenyl-hydrazine leads to,[33]



$C_6H_5-\underset{H}{N}-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-C_6H_5.$

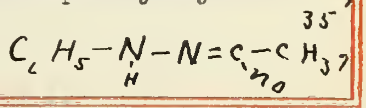
Fischer[5b] in his original investigation of nitroso-phenylhydrazine, considered that it was a normal nitroso compound because;(1) reduction leads to aniline indicating that the nitroso group is not attached to the benzene ring, and (2) in amines nitroso compounds are only formed with secondary amines, i.e. those with an imide hydrogen atom. From this he concluded that the secondary nitrogen of phenylhydrazine is the one to which the nitroso group is attached. He also pointed out that unsymmetrical secondary hydrazines which have no imide hydrogen atom do not form nitroso hydrazines, but are promtly decomposed on treatment with nitrous acid. In his opinion the formation of phenylazide on treatment of nitroso-phenylhydrazine with dilute alkali shows that water splits out between the nitroso and the amino group , again showing that the nitroso group is attached to the secondary nitrogen atom.

Thiele[30a,b], in view of new evidence, did not entirely agree with Fischer. He considered that there had to be some sort of tautomerism to account for some of the facts observed. If the structure of nitroso-phenylhydrazine were accurately expressed by $C_6H_5\underset{NO}{N}—NH_2$ under all conditions it would be hard to avoid the assumption that the formation of a sodium salt is due to the activation of <u>one</u> of the <u>two</u> hydrogen atoms of the amino group— an assumption that seems hardly reasonable. Furthermore Thiele pointed out that the quantitative elimination of N_2O from the phenylhydrazine derivative by simple heating is difficult to understand on the basis of the Fischer formula alone. Moreover, both benzaldehyde and acetaldehyde do not react normally with nitroso-phenylhydrazine, but yield the tetrazine,



$$\begin{array}{l} C_6H_5-N-N{=}CH-C_6H_5 \\ \quad\;\;\; | \\ C_6H_5-N-N{=}CH-C_6H_5 \end{array}$$

34, and

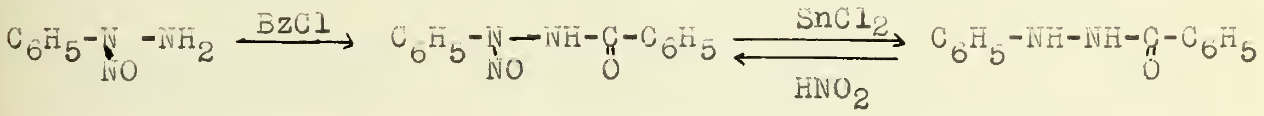


$$C_6H_5-\underset{H}{N}-N{=}\underset{NO}{C}-CH_3$$

35 ?

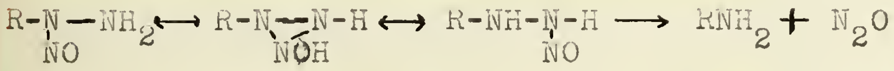
respectively. Curtius found that nitroso-benzylhydrazine which also forms a sodium salt and in other respects is closely related to nitroso-phenylhydrazine in properties forms normal condensation products with the same aldehydes.[31]

Thiele[36] found that the elimination of N_2O is common to both the aromatic and the aliphatic primary hydrazines, while not a trace of N_2O is eliminated from the secondary hydrazines such as nitroso-di-benzylhydrazine. Thiele and Sieglitz[37] explain the reaction of benzoyl chloride on nitroso-phenylhydrazine by;



$$C_6H_5-\underset{NO}{N}-NH_2 \xrightarrow{BzCl} C_6H_5-\underset{NO}{N}-NH-\underset{O}{\overset{}{C}}-C_6H_5 \underset{HNO_2}{\overset{SnCl_2}{\rightleftarrows}} C_6H_5-NH-NH-\underset{O}{C}-C_6H_5$$

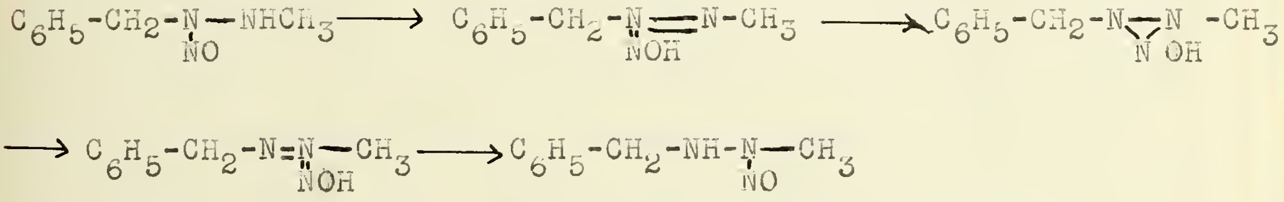
All of these facts confirm Fischer's conclusion that the nitroso group is attached to the secondary nitrogen atom as one form of the nitroso compound, but, to explain the formation of N_2O and other reactions observed, it appears that we have to agree with Thiele in his assumption that another form of the nitroso compound consists of a three membered ring[36,37] which exists as an intermediate form in some of the reactions encountered. The formation of azides and the elimination of N_2O from nitroso hydrazines would then be explained by the following steps;



$$R-\underset{NO}{N}-NH_2 \longleftrightarrow R-\underset{NOH}{N}-N-H \longleftrightarrow R-NH-\underset{NO}{N}-H \longrightarrow RNH_2 + N_2O$$

Bamberger[32] suggested yet another form which may exist as a tautomer of the original Fischer formula, because he found that nitroso-phenylhydrazine forms a copper salt which on treatment with either acetic acid or ammonia yields a compound of the formula; $C_6H_5-N-\underset{O}{N}-OH$ or $C_6H_5-\underset{O}{N}-NOH$. Kizis[37], one of Thiele's

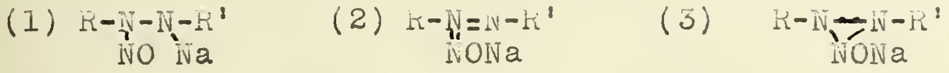
students, pointed out that the ready transformation of α-nitroso-α-benzyl-β-methylhydrazine to α-nitroso-α-methyl-β-benzylhydrazine as well as the formation of α-nitroso-α-methyl-β-benzilidinehydrazine by oxidation of α-nitroso-α-benzyl-β-methylhydrazine affords a strong proof of the existence of the three tautomers mentioned, since the rearrangements above may then be readily shown by the following reactions and rearrangements;



$$C_6H_5-CH_2-\underset{NO}{N}-NHCH_3 \longrightarrow C_6H_5-CH_2-\underset{NOH}{N}=N-CH_3 \longrightarrow C_6H_5-CH_2-\underbrace{N-N}_{N\;OH}-CH_3$$

$$\longrightarrow C_6H_5-CH_2-N=\underset{NOH}{N}-CH_3 \longrightarrow C_6H_5-CH_2-NH-\underset{NO}{N}-CH_3$$

The sodium salts of such compounds can then be expressed by either of the following three formulae;



$$(1)\; R-\underset{NO}{N}-\underset{Na}{N}-R' \qquad (2)\; R-\underset{NONa}{N}=N-R' \qquad (3)\; R-\underbrace{N-N}_{NONa}-R'$$

It is very difficult, if not impossible, to determine at the present time which of these three possible forms exist and which is the one that is found as the major product at any time. Chemical reactions offer little hope for the solution of this problem and physical methods have so far not been developed far emough to warrant their use in the case of nitrogen compounds of this type. An interesting confirmation of the assumption that the oxime form exists in the case of nitroso hydrazines is brought out through the fact that secondary nitroso hydrazines give an intensive blue color with ferric chloride in aqueous solution, a green color in alcoholic solution, and a red solution in solution of a non-dissociating solvent such as benzene, chloroform, and ether.[37] Alternate addition of water or alcohol brings about the

corresponding changes of color. This behavior seems to indicate rather definitely that the color is due to a strong hydroxyl ion formation in aqueous solution, a lower one in alcoholic solution, and the absence of this dissociation in such solvents as benzene and ether. The same color changes are produced in the case of the nitroso derivative of symmetrical diisopropyl-hydrazine although the color rapidly fades because of the rapid reduction of the ferric salts formed. These color changes can hardly be understood on the assumption that the Fischer formula is the only form in which these compounds exist. Although the proof is not yet conclusive it appears very likely that the salts of nitroso-hydrazines exist either as formula (2) or as (3) page 15, while the nitroso-hydrazine as such may normally exist mainly in the form assumed by Fischer.

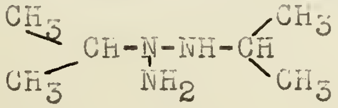
Nitrous acid reacts with symmetrical disubstituted hydrazines in two different ways. In most cases the mono-nitroso compound is formed[39]. In some cases, however, especially where acid salts of the base are stable, the dinitroso compound is formed if an excess of nitrous acid is employed. The mono-nitroso derivative may also be formed by the alkylation of the corresponding primary nitroso hydrazine[39].

The more interesting of the two types of nitrsoso compounds of symmetrical hydrazines is the di-nitroso derivative because it decomposes readily to form an azo compound and 2 mols of nitric oxide. This reaction takes place even in the cold in the case of the dinitroso derivative of hydrazomethane.

In the case of symmetrical diisopropylhydrazine, the mono-nitroso compound has, so far, been the only nitroso compound isolated. The fact that there is, in the case of the derivative prepared with acetic acid and an excess of sodium nitrite, always a considerable amount of evolution of gas even after the excess of acid has been neutralized may indicate that there is always formation of a small amount of the di-nitroso compound which would probably be very unstable and decompose before it could be isolated. Cooling slows down the gas evolution but does not stop it, and on warming the reaction continues at the former rate for several hours before finally slowing down and stopping entirely.

The properties of the nitroso compound agree, in the main, with those of other nitroso compounds described in the literature. The intensely blue color with ferric chloride, and the Lieberman reaction are found here, as in other nitroso compounds. Peculiarly enough, however, nitroso-symmetrical diisopropyl-hydrazine yields a sodium salt when treated with a concentrated solution of alcoholic sodium hydroxide. It is impossible to say at this time which of the structures advanced for such compounds (page 15) is the most probable one for this sodium salt, but it seems reasonable to hold that the oxime structures advanced by Thiele and Bamberger are more likely to be the ones found here than the formula assumed by Fischer.

Reduction of the nitroso derivative leads to ammonia and symmetrical diisopropyl-hydrazine instead of to the amino compound,



$$(CH_3)_2CH{-}\underset{NH_2}{\underset{|}{N}}{-}NH{-}CH(CH_3)_2 .$$

When the dry hydrochloride of the hydrazo compound is mixed with an excess of copper oxide, a peculiar sweetish odor is observed in about 15 minutes. In the course of an hour, if the excess of copper oxide is not too great, some moisture may be observed on the crystals. By next morning the mass is distinctly moist while the odor has become much more noticeable. After 3-4 days the mass is so wet that it may be poured from the flask in which the oxidation took place. After another day or two the reaction mixture in the original flask is distilled in a water bath. If the heat is applied slowly the ruby red crystals of an unstable copper salt which is first observed on the second or third day of the oxidation process, are found to change suddenly from red to greenish white at 88.5°. At the same time the oxidation product distills over as a yellow oil of a nauseatingly sweet odor. From 92-98° the distillate is composed largely of water which forms a separate layer underneath the oil layer.

The yellow liquid is readily dried over calcium chloride and is pure after one fractionation. The analyses and the molecular weight determinations show that the compound has the empirical formula, $C_6H_{14}N_2$. This formula applies to 2,2'-azobispropane and to the tautomeric acetone isopropyl-hydrazone. The determination of the structure of this compound constituted one of the most difficult parts of this investigation.

Aromatic azo compounds have been known for almost a century and have been thoroughly studied.[40]

Mixed aromatic-aliphatic azo compounds are known and are interesting because they often change over very readily to the

tautomeric structure[43].

Hydrazines of the type represented by symmetrical dibenzylhydrazine are usually considered as aliphatic hydrazines although their properties differ considerably, in some cases, from the purely aliphatic compounds represented by such compounds as symmetrical di-methyl-hydrazine and the hydrazo compound prepared in this investigation. The difference in properties is probably due to the proximity of the phenyl group. Symmetrical hydrazines of all types tend to yield stable, slightly colored or colorless azo derivatives.[44]

None of the azo compounds so far known are very closely related to the product to be expected on mild oxidation of the hydrazo compound derived from dimethyl ketazine. Azo methane is is the only homologue of 2,2'-azobispropane known so far. It has a very faint straw color in the liquid state, but is colorless as a gas (hence often erroneously called a colorless compound).[39] As is indicated by a boiling point of only 1.5°, its properties may differ considerably from those of the higher homologues because it is a well known fact that the properties of the first members of a homologous series are often markedly different from those of member with five or more carbon atoms.

The light straw color that is observed in every specimen prepared, the neutral reaction, the immiscibility with water, dilute alkali and dilute acid, and the unexpected stability towards hydrolyzing agents which makes it necessary to employ a solution of 1 part of water to 1 part of concentrated hydrochloric acid if the hydrolysis is to be completed within an hour of

boiling under reflux, all indicated that the oxidation product is actually the azo compound. An examination of the type of tautomerism showed that the properties mentioned,although they led to a strong presumption that the azo compound had been formed, did not absolutely exclude the possibility that the substance might be the hydrazone in spite of indications to the contrary. The following discussion shows what basis there was for any uncertainty in regard to the structure of the oxidation product.

Aliphatic azo compounds tend to decompose in two different ways. One is an actual decomposition, the other is a rearrangement. (1) Azo compounds may rearrange from the azo to the hydrazone structure;

$$-CH_2-N=N-R \longrightarrow -CH=N-NH-R$$

(2) Through elimination of one molecule of nitrogen gas, azo compounds may decompose to form hydrocarbons;

$$R-N=N-R \longrightarrow R-R + N_2$$

Among cases so far observed the hydrazone seems almost always to be the more stable form, although , in the case of symmetrically substituted hydrazines the azo is usually stable enough to be isolated, while some, like azomethane are stable enough to withstand rather high temperatures without showing any sign of rearrangement to the hydrazone form.

Fischer[43a] was the first to observe a case of this kind of isomerism when he noticed that acetaldehyde-phenylhydrazone is formed readily when phenylazoethane is treated with acids or alkali. In many cases,isolated since,it has not been possible to isolate

the azo compound that is supposed to be an intermediate in the oxidation of a symmetrical hydrazine to the hydrazone that is finally isolated.[43]

In the case of diphenyl and triphenyl methane derivatives the azo compound is also not stable, but in these cases the composition of the final products shows that the second type of decomposition of azo compounds has taken place, i.e. nitrogen gas and a hydrocarbon are the products.[39]

In the case of Kischner's synthesis of hydrazones of the type, $R-NH-N=R$, the intermediate azo compound is not isolated [44]. Azo isobutyric acid and the dinitrile from which it is formed are stable because they cannot rearrange according to the first type of rearrangement. When, however, carbon dioxide is eliminated from the compound it rearranges immediately to the hydrazone.[41c] Whether the same rearrangement would take place if two, instead of one mol of carbon dioxide , were eliminated could not be shown by Thiele.The compound obtained on oxidation of the hydrochloride of 2,2'-hydrazobispropane, shows that the rearrangement would not have taken place if Thiele had been able to eliminate both molecules of carbon dioxide at the same time.

From a consideration of the rearrangements just discussed, it may readily be seen that a compound which, like the oxidation product under discussion, may be refluxed for hours and may even be treated with sodium alcoholate for several hours at a time at 110° without any noticeable change, might well be mistaken for a hydrazone in spite of the other properties mentioned. Since absorption bands could not be de-

tected in the visible spectrum on examining the oxidation product for such bands, and since the refractive constants for nitrogen in compounds have not been determined for compounds of this type with sufficient accuracy to make them useful in proving the structure of a compound like 2,2'-azobispropane, physical means did not seem to offer any hope of being able to prove the structure at all conclusively by their aid.

The only two feasily methods left now were;
(1)The preparation of a derivative of the oxidation product, and
(2) the preparation of the hydrazone itself by some other method. Of these, the first gave little hope of success since it became apparent,after a series of experiments, that no derivatives that would be of value in proving its structure could be obtained from the oxidation product. Possibly such derivatives may some day be prepared by methods that were not tried in this work. The second method held out equally small hope at first, in as much as, in spite of numerous trials under varying conditions no hydrazone could be isolated although the odor of a new compound could be noted in a number of trials.

Reddelien's method[46] of condensing aromatic amines with aldehydes and ketones to form aniles proved to be the only method that gave a good yield of the hydrazone.

Zinc chloride is very often used as a dehydrating agent since it is one of the most hygroscopic of substances. Moreover, the vapor pressure of water over moist zinc chloride at 25° is only 0.85 mm while at 50° it is still only 2.99 mm. Since the absorbed

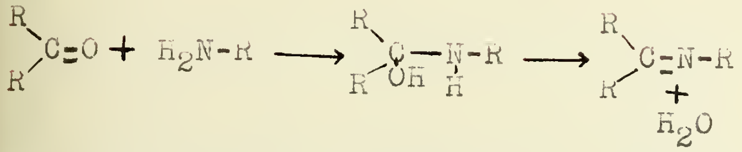
water is not given off until the melting point is reached at 290-297°, this salt may, in many cases , be used as a dehydrating agent from which the the dried substance may be distilled directly. Naturally, the tendency of zinc chloride to form complex salts with amines and many other substances must be taken into account.

Reddelien made the peculiar observation that, in the preparation of aniles, the zinc chloride does not act so much as a dehydrating agent as in the capacity of a catalyst; i.e. the salt does not "bind" the water, but immediately liberates it as steam at the temperature of 170-180° employed by this investigator in his condensations. Thus, in the preparation of benzophenone-anile, he employed 1/40 mol of zinc chloride to 1 mol of each of the other reagents, and yet obtained a very satisfactory yield of the anil . There is here then here some sort of catalytic action similar to that of iodine when it is used as a condensing agent in the preparation of the same type of compounds.

Another interesting observation that Reddelien makes in this connection, is the fact that the zinc chloride acts as a catalyst only in cases in which the bases concerned form a definite compound with the zinc salt. If such a salt is not produced the zinc chloride acts simply as a dehydrating agent; one mol of the zinc salt must be used to one mol of the base and the reaction must be run at a higher temperature than in those cases where the zinc salt acts as a catalyst.

The work of Zoeppritz and Dimroth[47] may throw some light on the mechanism of this type of condensation reaction. They claim

that anile (and presumably also hydrazone) formation takes place in two steps;


(R = aromatic.)

They isolated the intermediate product. It is very easily decomposed by heat either into the original substances or into the desired anile. The fact that the first step could not be observed in the preparation of acetone-isopropyl-hydrazone may mean that in this case, this substance is so unstable that it immediately eliminates water and changes to the hydrazone even at 40-60° at which this reaction is run with best yields.

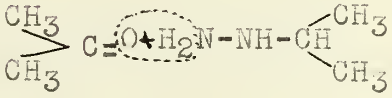
Contrary to the experience of Redelien who had to heat his reaction mixtures to 170-180 degrees, it is found that the reaction mixture of acetone, zinc chloride,and primary isopropyl hydrazine heats up spontaneously and has to be cooled to keep the temperature from rising above 40-50 degrees with too much loss of acetone on boiling. Zinc chloride readily forms a compound with the primary hydrazine, but, as only a small amount of zinc salt is employed the amount of complex salt formed does not greatly lower the yield of hydrazone obtained. The product is distilled directly without attempting to filter the zinc salts that are found in the mixture. There is a slight lowering of yield due to this distillation from the salts, but this loss is not as great as that due to attempting to filter off the gelatinous zinc salts that are formed in the reaction. The product obtained on distillation is mixed with an equal volume of dry ether and dried over anhydrous

sodium sulphate for 3-4 days. Distillation now gives a yield, sometimes as high as 70% of the calculated yield of the colorless hydrazone boiling between 125-and 135°. On refractionation of this part almost all of the product comes over between 132 and 134°. Thus prepared the hydrazone is a colorless, basic, liquid with stinging menthol odor. It is extremely sensitive to any hydrolyzing agent, even water readily hydrolyzing it into its original components. This explains why it was so difficult to obtain the product in the earlier experiments made in an attempt to produce this hydrazone as a part of this investigation. All attempts to make the benzoyl, the phenylmustard oil, the cyanic acid, or the hydrocyanic acid derivatives of the hydrazones failed for the same reason. The product obtained was always the derivative of the primary hydrazine — one of the hydrolysis products. The hydrazone is the first one that has been isolated among the purely aliphatic series of nitrogen compounds while the azo compound is the second azo compound that has been prepared in this series. The azo and hydrazone stand also as the first case in which both the azo and the hydrazone corresponding to a single aliphatic symmetrical hydrazine have been isolated.

A comparison of the properties of the two tautomers leaves no doubt as to the structure that must be assigned to each. For convenience these properties are arranged in tabular form as Table I on page 26.

TABLE I.

Tabular Arrangement of the Most Important Properties of 2,2'-Azobispropane and Acetoneisopropyl-Hydrazone.

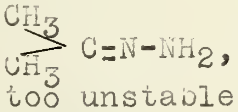
Property	2,2'-Azobispropane	Acetone-Isopropyl-Hydrazone
Color	Faint Straw	Colorless
Boiling Pt.	88.5°	132-4°
Density t/4	.7408	.8223
Mol.Wt	114 (110,119)	114 (105,108,104)
Mol. Volume	154	138.7
n_D (Abbe)	1.3890	1.4360
Carbon % (63.15 Calc)	63.18,63.02,63.02	62.69,63.00
Hydrogen%(12.28 ")	12.03,12.05,12.46	12.47,12.55
Nitrogen%(24.56 ")	24.67	24.98, 24.34
Odor	Nauseatingly Sweet	Stinging,Menthol
Synthesis	Oxidation of 	
Behavior towards;		
Water	Insoluble	Soluble.Hydrolysis
Dilute acids	"	" "
Dilute base	"	Solution and slower hydrolysis
Conc. Alkali and Heat	Partial Rearrangement to hydrazone	No change to azo, any conditions .
Reduction	Easily to Hydrazo	Easily to Hydrazo
Oxidation	Stable ordinary,weak.	Decomposition.Red color.

When the azo derivative of symmetrical diisopropyl-hydrazine is boiled under reflux with 50:50 hydrochloric acid and water the supernatant oily layer of azo compound gets thinner and thinner and after about 30 minutes disappears entirely. After about 30 minutes more the the condenser is arranged for distillation and the acetone distilled off . The rest of the liquid is distilled off under the vacuum of a water pump until the residue has become syrupy . If the syrup is now cooled in an ice bath the whole mass turns solid. The fine crystals are filtered off rapidly by suction and the filtrate concentrated some more and the same procedure repeated until only a few c.c. of filtrate remain. The last residue of the hydrochloride of primary isopropyl-hydrazine may be removed from this filtrate now by adding a few drops of alcohol and several c.c. of ether. Unlike the hydrochloride of the symmetrical hydrazine the residue should not be evaporated to dryness because the hydrochloride apparently begins to decompose before it crystallizes out of a syrupy solution like the one obtained on concentration of the hydrolysis mixture. The hydrochloride is purified by recrystallization from a very small amount of alcohol, or from a mixture of a very small amount of alcohol to which while hot ether is added to the first permanent cloudiness. The hydrochloride prepared thru hydrolysis of the azo compound by conc. acid as described above is very hygroscopic, while the one obtained by either of the other methods mentioned in the next two paragraphs is not hygroscopic or at most only slightly so. Both salts yield the same base on treatment with a concentrated solution of sodium hydroxide. Probably the hygroscopic salt is

the acid salt since it is prepared in the presence of the fairly concentrated acid and since the acid salt is usually the more hygroscopic salt. Because of the difficulty of working with an extremely hygroscopic salt, no attempt was made to analyze the hygroscopic salt, but the neutral salt was analyzed and proved to be normal.

Primary isopropyl-hydrazine is also obtained when the hydrazone synthesized above is hydrolyzed by dilute acid or even by water. The products formed here, as in the case above, are acetone and the primary hydrazine. The acetone was identified in each case by means of the benzilidine derivative, by means of the iodoform test, and finally by the sodium nitroprusside color test.

A third and best method of preparing the same primary hydrazine consists in reducing an equi-molecular mixture of acetone, hydrochloric acid, and hydrazine hydrate in exactly the same manner that the symmetrical disubstituted hydrazine is prepared. The isolation of the hydrochloride is accomplished in the same manner for any of the three methods described.

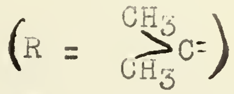
The simple hydrazone,  $\begin{matrix}CH_3\\CH_3\end{matrix}\!>C{=}N{-}NH_2$, was prepared by the method of Curtius[11], but is too unstable to be used in obtaining the physical constants of this class of nitrogen compounds.

The dibenzoyl and the phenylthiosemicarbazide derivatives are readily prepared and were analyzed in connection with the positive identification of primary isopropyl-hydrazine.

Primary isopropylhydrazine may be liberated from the

hydrochloride in the usual manner by very concentrated alkali which causes it to rise to the surface to form a supernatant layer of yellow oil. This layer is then dried first with fused potassium hydroxide and then with aluminium amalgam. The amalgam is slow in its action, but the base is thoroughly dried by it. Metallic sodium is found to be satisfactory and very fast in its action in drying the symmetrical hydrazine, but it seems to decompose part of the primary hydrazine if an attempt is made to use it here. In every case the base produced from the hydrochloride constantly gives off tiny bubbles of gas even when the hydrazine has been thoroughly dried and distilled in an atmosphere of nitrogen. Kischner[45] reports the same behavior in the case of heptyl and octylhydrazines. No satisfactory analyses were obtained on the free base and a determination of its physical constants is evidently useless since refractive index determinations show that the compound gradually decomposes. The boiling point is between 104° and 106° for the freshly distilled base. The primary hydrazine was definitely identified through analyses of the hydrochloride and of the dibenzoyl and phenylthiosemicarbazide derivatives.

In as much as the series;



$\left(R = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C=\right)$

$R=N-N=R$, $R=N-NH-RH$, $RH-NH-NH-RH$, $RH-N=N-RH$, and $RH-NH-NH_2$ furnishes a rare opportunity for the study of closely related compounds differing in only small details, an attempt was made to determine as many physical constants as possible on all compounds that are stable enough to permit a reasonably accurate

determination of such constants. The results of these determinations, as far as completed, are here offered as they were obtained without any attempt at generalization. It is hoped, however, that, when the corresponding constants for other series of such compounds become available generalizations of value may be arrived at.

II EXPERIMENTAL

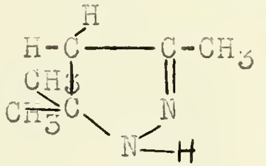
DIMETHYL KETAZINE.- This compound was prepared according to the method of Curtius and Zinkeisen[18b]. The yield was not satisfactory at any time. While the method, as given, gives a yield of 60-70% and a slight modification of the method, i.e. the use of a 25% excess of acetone, increases the yield to 70-75%, this yield can not be considered satisfactory in view of the high price of hydrazine at this time. The use of sodium hydroxide was abandoned for a while and sodium carbonate substituted for it but the yield remained the same.

A red oil was always obtained as a residue after the 128-135° fraction had been distilled off. The residue, when hot, ignites on contact with air, showing that the substance is very easily oxidized. The yield was too small however to permit isolation and identification of the oil.

ATTEMPTS TO REDUCE THE KETAZINE.- Although not much hope of success was entertained since a number of chemists had tried and failed to reduce dimethyl ketazine, another series of attempts were made to reduce the ketazine with common reducing agents after the reduction products were known through reduction of the ketazine by a method described later. It was hoped that a knowledge of the compound to be expected would permit the identification of a small amount of hydrazo compound that might have escaped the attention of earlier investigators. Sodium as amalgam, and as metal in alcohol; aluminium as amalgam, and as free metal in the presence of potassium hydroxide, gave traces of reduction compounds

but the hydrazo compound could not be identified among them. Zinc with various acids, iron with acids, and stannous chloride failed to give any reduction products of the ketazine.

3-METHYL-5-DIMETHYL PYRAZOLINE, .- When a few drops of benzoyl chloride were added to a few c.c. of the reduction mixture obtained in one of the unsuccessful attempts to reduce dimethyl ketazine, a crystalline compound melting at 228-9° was obtained. Melting point, appearance, and analysis showed that the substance is the benzoyl derivative of 3-methyl-5-dimethyl pyrazoline which was originally prepared by Curtius and Zinkeisen[18b].



Analysis:

Calculated, for $C_{13}H_{17}O$, N = 12.96%

Found; (Dumas) N = 12.92%

The acid formed during the reaction and by hydrolysis of benzoyl chloride is thus strong enough to effect the rearrangement studied by Curtius, Frey and Hofman[18d], and Franke[18c].

REDUCTION OF DIMETHYL KETAZINE.- Skita's method of reduction by hydrogen under the catalytic influence of colloidal platinum protected by gum arabic was finally used with complete success in the reduction of the azine.

The apparatus used at first was modelled after the one described by Skita[25a], but was later modified so as to be less expensive and, especially, also less space consuming. The use of the troublesome pressure regulator of Skita was also avoided. The final form of the apparatus is shown in Figure I.

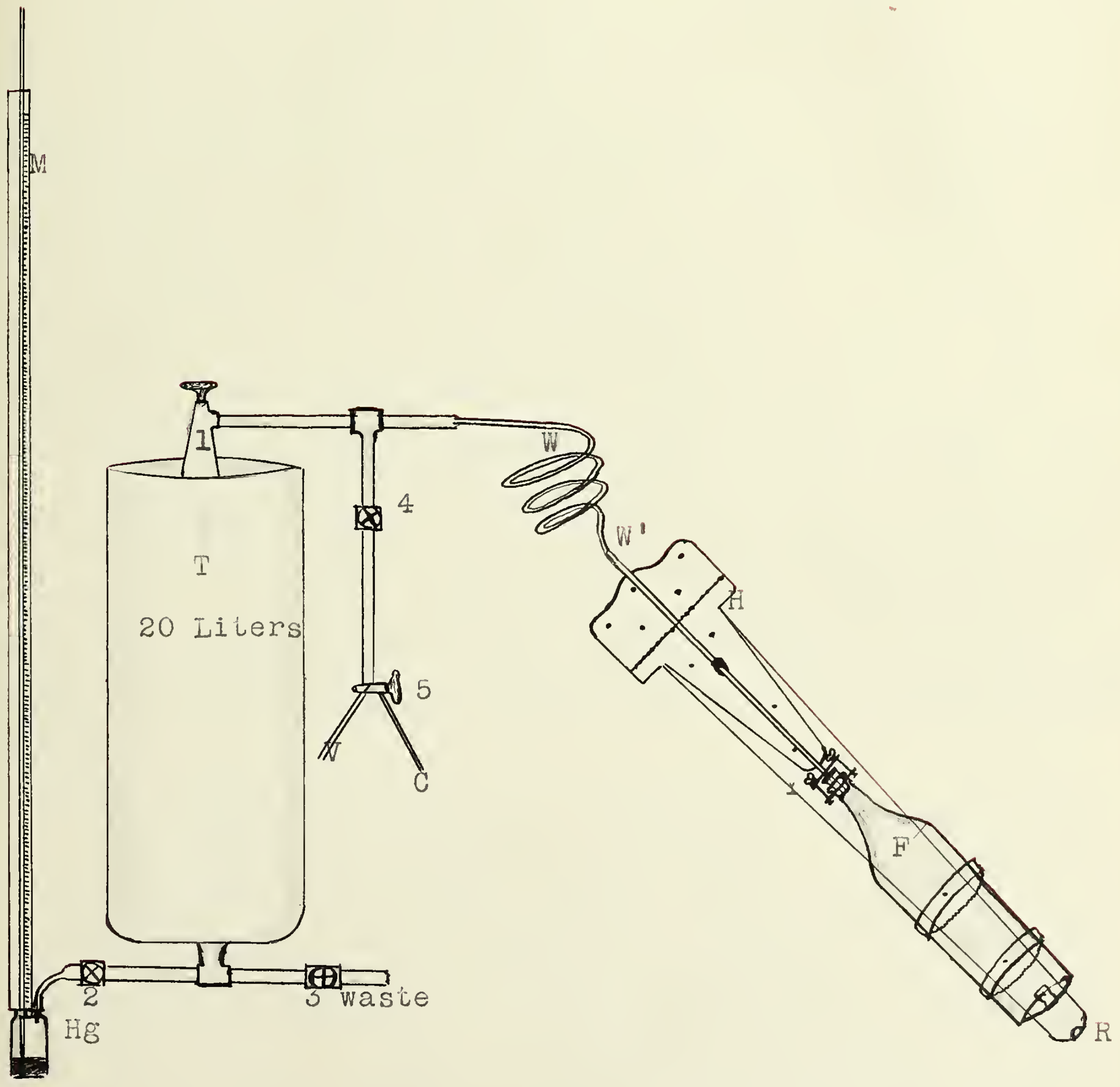


Figure I

The open-top mercury manometer has a length of 200 cm so that a height considerably in excess of 180 cm of mercury or over two atmospheres excess pressure may safely be employed in the apparatus. The capacity of the tank,T,was so regulated by m means of a small amount of distilled water that was placed in the bottom to seal all stopcocks and at the same time to pro-vide for a flexible capacity of the gas holder. When the capacity is about 20 liters the average running pressure of the apparatus will be such that the drop of 1 mm in pressure is equal to 10 c.c. as an average. The exact values represented by a change of pressure of 1 mm at any desired temperature and any desired total pressure (atmospheric plus extra) are read directly from a chart made when the tank was calibrated with the water level fixed permanently. In this way it is possible to use only the theoretical amount of gas to complete the reduction desired, thus avoiding incomplete reduction through stopping the shaker too early, or over-reduction through adding more hydrogen than desired.

The shaker is fastened to the wall by a strong hinge. By this arrangement the shaker occupies little space when in use, and practically no space when not in use as it may be folded back against the wall. The hinge and board are fastened to the wall at an angle of about 45 degrees as shown in the figure. This angle is found to provide the most efficient stirring and shaking when the arm is swung back and forth by a common motor driven shaker. The rocking arm of the shaker is fastened at the point,R.

The flask is fastened in a rapid and very satisfactory manner by means of two screen door springs that are hooked into rings behind the board. To prevent poisoning of catalyst due to contact of the liquid with the brass or copper tubing, the coiled tube is cemented into a piece of glass tubing which then passes through the rubber stopper of the pressure flask. The rubber stopper is held in place securely even under more than 2 atmospheres of extra pressure, by means of the yoke clamp, Y.

PROCEDURE.- In making a reduction run for the first time the acetylene tank, T, is first evacuated, the open end of the copper coil ,WW', being closed by fastening into the empty pressure flask. When the pressure has dropped as low as the water pump will take it (20-30 mm), the three-way stopcock ,5, is turned so as to connect with "C" instead of with "V". "C" is connected to the hydrogen cylinder by means of a short length of rubber pressure tubing of not too great strength so that in case the pressure is accidentally raised too high due to carelessness in manipulation of the valves or to stoppage of some passage, the pressure will be indicated by the bulging of the tubing and the eventual blowing out of the tubing. When the tension of the tubing, as felt by the hand, indicates that there is a slight pressure in the system, the gas is turned off again, the three way stopcock turned back to "V", and the evacuation repeated. When again evacuated and refilled with gas until a slight pressure is indicated by the tubing leading from the cylinder to the tank, the valve 2 which has been closed up to now, is opened and the pressure in the tank permitted to rise slowly to a total

pressure of about 2500 mm of mercury. The valves 1 and 4 and the stopcock 5 are then closed and the flask disconnected from the tubing and charged for the run. The usual charge consists of 50 c.c. of ketazine, 100 c.c. of water, 100 c.c. of 13% hydrochloric acid, 10 c.c. of a 10% solution of platinic chloride, and .5 g of gum arabic dissloved in hot water. To this mixture is then added the "seeding" colloid prepared either according to the directions of Skita by heating a few cubic centimeters of a palladous chloride solution to boiling and then, while removed from the flame,allowing a slow stream of hydrogen gas to pass through the solution to reduce the metal to the colloidal state, or by partially reducing 2-3 cc of chloroplatinic acid by making it alkaline, heating to boiling,and adding a few crystals of hydrazine chloride or of the hydrochloride of symmetrical diisopropyl-hydrazine . As soon as the mixture turns black it is rapidly poured into the pressure flask where the alkali is neutralized by the acid present. The flask is then connected to the system again and evacuated until the acetone starts to boil. The air is then sufficiently removed to permit the reduction to proceed. The gas is admitted to the flask by opening valve 1 as soon as possible after the valve 4 has been closed to cut off the vacuum. If the acetone vapors are permitted to condense, in any amount, in the coiled tube, the catalyst may be poisoned by this liquid when the gas pushes it back into the flask in course of the run. For this reason the gas should be turned on as soon as possible after the evacuation is completed. If the desired amount of pressure is now in the system the shaker is started and the total pressure,

and temperature read and recorded.

For a few minutes little, if any, absorbtion is noticed. If the acetone has been properly purified absorbtion will start in a few minutes and grow steadily more rapid for about an hour when it reaches its maximum and gradually slows down only to stop enitrely when the ketazine has been all reduced to the symmetrical hydrazine. This may take only 3-4 hours if no anti-catalytic substance is present. Usually there will be enough of such substances present as impurities so materially slow down the run so that 6-8 hours are required, unless the shaker is stopped after the absorbtion slows down noticeably and more platinum solution added. The rate of reduction depends on the amount of catalyst present so that , presumably,the reduction could be carried out in much less than 3 hours if we were willing to use more platinum than necessary. Usually one additional addition of 10 c.c. of chloroplatinic acid sufficed to reduce a regular charge in 3-4 hours. In some such runs absorbtion took place at the rate of over 12000 c.c. an hour for over a hour at a time. The solution in the flask warms up considerably when reduction proceeds as rapidly as this. If it does not heat up to about 40 ° it is advisable to place a very small flame some 6 or 8 inches below the flask to heat it to the temperature of about 40° at which absorbtion takes place at the maximum rate. Should the temperature in any run rise to the boiling point of acetone the reduction would be materially slowed down because of the acetone vapor which would not permit the hydrogen to get in contact with the liquid rapidly enough to sustain the original rate

of reduction.

If an attempt is made to use the acetone of commerce disappointments are almost sure to come. In almost all cases in which the acetone is to be used in catalytic reduction processes it has to be purified to make it suitable for use. The impurity manifests itself during a reduction run by preventing absorbtion of hydrogen entirely, if there is much catalyst poison present, or, in case only a small amount of anticatalyst is found, the absorbtion may start but almost immediately reach a maximum, far below the maximum reached when pure acetone is employed, and then rapidly drop off until no gas is absorbed.

To purify the acetone the method of Shipley and Werner[49] was found satisfactory, If sodium iodide and acetone are refluxed for an hour or more a very concentrated solution of sodium iodide is obtained. On cooling the solution down to -10° or even to -15 ° . if convenient, the sodium iodide-acetone addition compound precipitates out as large reddish needles. These are sucked off rapidly on a large Buchner funnel without filter paper. The needles are so large that they do not pass through the funnel. The needles are then placed into a distilling flask and the acetone is distilled off. It practically all comes over between 56.5 and 56.8 at 750 mm and is apparently now entirely free from anticatalytic action. The filtrate and the residue of sodium iodide from the distillation are mixed and another small amount of acetone added. This mixture is refluxed as before and a second quantity of pure acetone obtained from it. If the acetone as obtained from stock is fairly pure, the purifying process may

be repeated as much as 5-6 times before cleaning the iodide.

To purify the sodium iodide so as to be able to use it again for similar work or for other reactions the acetone is all distilled off on a water bath. The wet residue is then poured into an enamelled pan where it is further dried by gentle heat. When thoroughly dry the heat is gradually increased until all organic matter has been carbonized. Thus ignited it is ready for use in acetone purification. For other chemical work it must obviously be purified by recrystallization before use.

A few early runs were run using the mixture of ketazine water, and catalyst as described on page 37. The reduction was found too slow however and the reductions as next modified gave better yields in shorter time.It was observed that the addition of chloroplatinic acid always produced a rapid rise in absorbtion. The question arose whether this rise could occur as suddenly as it did if the extra platinum added were the only factor that increased the rate of absorbtion of hydrogen. A small amount of hydrochloric acid was next found to have the same effect, in case no anticatalyst was present, as the addition of chloroplatinic acid. By adding small portions at a time the time of reduction was soon cut down to less than a day. The next step was to add the theoretical amount of acid,needed to salify all of the base formed , at the start. The first run failed because the platinum refused to be reduced to the colloidal state under these conditions. In subsequent runs the reduction was allowed to proceed for a few minutes and the acid then all added at one time. The yield was practically quantitative.

Since the results showed that the addition of the calculated amount of hydrochloric acid in one lot did not reduce the yields and even shortened the time required, the question of hydrolysis of the ketazine was eliminated. The next step forward was the use of a mixture of acetone and hydrazine hydrate instead of ketazine. This avoided the step that yielded the lowest yield -- the preparation of dimethyl ketazine. 2.2 mol of acetone, 1 mol of hydrazine hydrate, and 1 mol of hydrochloric with the original amounts of chloroplatinic caid, gum arabic and "seeding" colloid now constitutes a regular run after dilution with 100 c.c. of distilled water. In three runs on which the yields, by this method, were obtained, 25 g of hydrazine hydrate the following results were obtained,-

I. 25 g hydrazine gave 78 g of hydrochloride in 4 hours,
II.25 g hydrazine gave 80 g of hydrochloride in 3.5 "
III,25 g hydrazine gave 74 g of hydrochloride in 6 hours.

The salt was weighed after it had been recrystallized once from alcohol and had been kept on paper over night. Its melting point was 197-8 unsharp for each batch, a chlorine determinations by Mohr's method gave 23.8% Cl, and titration with N/10 iodine gave an average purity of 95.3% for the salt. These show that the salt was practically pure and the yield almost quantitative. The more usual yields lay between 88 and 95% however because the above runs were made on especially purified reagents. Even 90% is a highly satisfactory yield however when the isolation of the ketazine is avoided entirely.

When poisoning of the catalyst does occur, as shown by the phenomena described previously, the poisoning , if it is slight ,may often be overcome by the use of an excess of catalyst. If the poisoning be severe though it is best to recover the hydrazine as hydrochloride and as much of the acetone as possible and start out on a new run. The origin of the poison is often very difficult to locate, in fact, in many cases subsequent runs with the same reagents prove to be normal. In a number of cases where the catalyst lost its activity more and more, apparently through exhaustion of its catalytic activity, whatever that may be due to, attempts were made to revive the catalyst by shaking it in contact with air for varying periods of time. Even on shaking for as long as two hours no revival of activity could be detected in any case.

ISOLATION OF THE REDUCTION PRODUCTS.- When the theoretical amount of hydrogen has been absorbed, the valve 1 is again closed so as to save the gas in the tank for future runs and to avoid the preliminary evacuation of the tank. The flask is disconnected from the system and allowed to stand for a few minutes. If the colloid is still homogenous, and equal volume of acetone is added to the mixture and the contents of the flask shaken violently for a few minutes. The colloidal solution will now usually be broken up into large flakes which soon settle out, leaving the rest of the mixture clear. In many cases the colloid is found to have broken down while the reduction was still going on. In such cases, of course, no additional acetone is added. In either case it is best to let the mixture stand overnight when the clear

liquid may then be poured through a large pleated filter in a few minutes and the mass that has settled out will drain within an hour or less after it has been placed on the filter. If an attempt is made to filter the mixture immediately after the colloid has been broken or if suction is applied in an attempt to save time it is very difficult to filter at all as the black mass of flakes cannot be filtered under such conditions with any degree of satisfaction.

To isolate the reduction product, the solution is made acid to congo , unless already acid. In case acetone was used to break the colloidal state, the acetone is now recovered through distillation. The remainder of the solution is evaporated down in vacuum on a steam bath. As the solution becomes more and more concentrated fine long hairlike needles of the hydrochloride begin to crystallize out on the walls of the flask. If some lots of pure product are desired, the residual solution is now well cooled in an ice bath and the mass of crystals that separate out are filtered of by suction. The filtrate is concentrated further in vacuum and another lot of pure crystals obtained. Finally the filtrate is evaoprated to dryness to get the remainder of the hydrochloride since it is very soluble in water. If no special batches are desired the evaporation is carried to dryness in the first place and the time consumed in cooling and filtering saved.

RECOVERY OF THE CATALYST:- To recover the platinum the filter and black mass of precipitate are permitted to dry thoroughly before attempting to work with them. The dry filter is burned

over a porcelain dish. To keep from cracking the dish, it is best to hold the filter with a pair of glass rods until the ashes drop off into the dish. The ashes and carbon in the dish are then carefully scraped into a crucible and ignited with a blast lamp. The metal is next dissolved in aqua regia. The first solution is evaporated down on a water bath, water added, evaporated to dryness again, hydrochloric acid added, and evaporated again. This alternate treatment with water and with hydrochloric acid is repeated until the platinum solution has been evaporated three times with the acid. Water is again added and the final evaporation carried out in vacuum. The residue obtained now is dissolved in a few drops of water and finally diluted to the same color that the original solution had. It is now ready for use as a catalyst in reduction runs. The loss per recovery is small, but when the same platinum goes through dozens of runs the loss gets more and more noticeable.

SYMMETRICAL DIISOPROPYL-HYDRAZINE.- The hydrochloride obtained on evaporation of the reduction mixture is recrystallized a few times from small quantities of alcohol or from acetone, before liberating the base in case analyses are to be run on the sample obtained. If the base is to be used for the preparation of derivatives the purification is unnecessary. In either case the base is liberated by means of very concentrated sodium or potassium hydroxide. It floats as a layer of yellow oil. This is separated from the water layer and the latter extracted twice with ether. The oil and ether extract are united and dried for

at least 24 hours with fused potassium hydroxide. This removes most of the water. After the alkali drying is complete, the mixture is poured off the potassium hydroxide and into another tube. The odor of the oxidation product is easily noted along with the ammoniacal odor of the base. The final drying is done by freshly prepared aluminium amalgam prepared from clean pieces of aluminium foil and mercuric chloride. The amalgam is allowed to react with the base for a week or more. During this time the yellow color and the azo odor disappear as the oxidation products is reduced to the hydrazine again. This fact makes aluminium amalgam far superior to any of the oxide drying agents such as barium oxide and calcium oxide. The same result - drying and reduction - obtained very much more rapidly by metallic sodium but it is more difficult to get rid of the slimy sodium compounds that are formed during the drying and reduction. At the end of the drying period, the base is carefully poured off the aluminium hydroxide and unchanged amalgam and distilled from a small distilling flask thru which dry nitrogen gas has been passing for some time, to drive out all of the air. The stream of gas is kept going during the distillation. When the temperature reaches 124° the first reciever is removed after the flame has been removed to prevent loss during the change of receivers. Before heating again the stream of nitrogen is sent through the new reciever for about 10 minutes to remove all air. On again heating and distilling the remainder of the base it is found to practically all come over between 124 and 125° as a mobile, colorless liquid of ammoniacal odor. Titration by iodine

or by hydrochloric acid shows that the base is not yet quite pure (97-8% purity.). To obtain a very pure sample for determination of the various physical constants, the last trace of oxidation product (azo compound) is removed by using a small absorption apparatus of the type described by Noyes ~~and Coleman~~[53]. After the 124-5° fraction has been collected in this small reciever under the usual precautions, the dry nitrogen gas is allowed to continue bubbling through the absorber until the index of refraction remains constant during 15 minute intervals. There is some loss of symmetrical hydrazine along with the azo compound that is volatilized , but the loss is far smaller and the purity greater than by any other method tried. Analyses, by rapid iodine titrations, showed that the purity of the base is about 99.5%. To preserve the pure product, the absorber is emptied, with the gas still passing, into a small nitrogen filled bulb which is then rapidly sealed by a blast lamp. Apparently the base thus collected may be kept indefinitely, while in contact with air it is immediately oxidized partially. Even in well stoppered tubes the decomposition is considerable.

The pure base boils at 124.5° at 751 mm pressure, and is a colorless mobile liquid with an ammoniacal odor. It reduced ammoniacal silver nitrate, aqueous silver nitrate, and Fehling's solution in the cold.

The index of refraction (Abbe instrument.) is $\eta_D^{24} = 1.4125$

The density, found by picnometer, is D31/4 ....0.7712

Methods of Analysis.- The most convenient methods of analysis of the free hydrazines, and the methods most commonly used in this investigation, are volumetric methods. Iodine tirations according to the method of Stolle[50] are especially convenient and accurate. The reaction proceeds according to;

$C_6H_{16}N_2 + I_2 \longrightarrow C_6H_{14}N_2 + 2\ HI$. The oxidation product is the azo compound, identified by odor, index of refraction, and boiling point. Stolle assumed that the use of his method in the case of primary hydrazines lead to hydrazo derivatives. In view of the fact that in the present work the hydrazo compound is titrated with iodine under the conditions employed by Stolle, it is far more probable that the reaction in the case of primary hydrazines proceeds according to;

$2RNH\text{-}NH_2 + 2\ I_2 \longrightarrow R\text{-}R + 4\ HI$, which is the normal behavior of primary hydrazines towards mild oxidizing agents. Another volumetric method that gives good results,-results that may later be checked by an iodine titration on the same sample,-consists in titration by N/10 hydrochloric acid using methyl red as indicator.

To check the results obtained by titrations, combustion analyses were also resorted to and proved to be very troublesome at first. The compound, as well as most of its derivatives, is very easily partially oxidized, but some of the products formed in the partial oxidation seem to be very stable. They pass over the long layer of copper oxide without change unless the oxide has been heated to a pink color. Even then the decomposition must be very carefully regulated to prevent pushing

the gases over the oxide at too rapid a rate. In the Dumas nitrogen determinations the results were always high if the decomposition proceeded too fast for even as little as a minute of time. On the other hand, carbon and hydrogen determinations were always low under the same conditions. After more than twenty failures with the usual combustion furnaces, an old furnace was remodelled to fit the special conditions. The heavy iron yokes supporting the combustion tube were replaced by a 40 inch length of angle iron. The extra length of bed permitted the use of an extra burner outside of the end supports, thus making the furnace about 4 inches longer than it had been. The tiles along both sides of the bed were so arranged that they are readily removable in case decomposition threatens to become too fast. Six inch sections of asbestos board are used as a roof for the furnace. By removing the section above the sample it may be rapidly cooled. To provide for cases in which the removal of the tiles and roof sections does not bring the decomposition into immediate and accurate control, ice is kept available so that on an instant's notice a small block of ice may be rubbed along the lower side of the bed. This radical cooling was found necessary on many occasions. The tendency to very rapid decomposition is very pronounced in nearly all of the compounds studied. With the furnace as described and with very slow and careful decomposition the results are as reliable and accurate as those on more easily burned substances. Although the use of oxygen during the decomposition in carbon and hydrogen determinations results in small explosions, one of which was severe enough to wreck the combustion tube, air may be

safely used to provide for a constant and even movement of the gaseous decomposition products.

Analyses: Calculated for $C_6H_{16}N_2$, C,62.08; H,13.80; N,24.14%

Found; C = 62.39; 62.17; H= 13.97,14.31; N = 24.30,24.54%

An attempt was made to use the Kjehldahl method for the nitrogen determinations, but the usual method, of course, fails entirely since the nitrogen is all given off as free nitrogen. If an attempt is made to reduce the compound to be analyzed bt the Kjehldahl method, the disappointing fact is revealed that the substances do not seem to be reducible by any ordinary means. A large number of attempts were made to reduce the hydrazo compound to the primary or possibly secondary amine, but no method tried gave any sign of a reduction to the amine. This great stability towards reducing agents explains the failure of the Kjehldahl method for these compounds.

A wet method for the determination of the per cent of nitrogen in these compounds was worked out in the course of this investigation. Except for slight modifications to fit it to special conditions, the method and the apparatus used is similar to a number of such methods developed in the past. A bulb of about 25 c.c. capacity is blown at the bottom of an ordinary test tube, if no flask of such shape is available in stock. A one hole rubber stopper fits into the neck of the flask. A small dropping funnel is sealed into an 8 mm piece of tubing in such a way that the tip of the dropping funnel stem projects well down into the flask when the 8 mm tubing is passed just through a hole in the rubber stopper fitting into the neck of the de-

composition flask. Above the ring seal a short sidetube is sealed on the stem of the dropping funnel. This sideneck is the opening through which carbon dioxide gas enters the apparatus to sweep out the air. Between the ring seal and the rubber stopper, a sideneck is sealed to the 8 mm tubing. This opening serves as outlet for the decomposition products and for the carbon dioxide used in rinsing the decomposition flask.

To determine the per cent of Nitrogen contained in an unknown substance, the sample is weighed into the decomposition flask and about 10 c.c. of water added to it. The stream of carbon dioxide gas from a Kipp generator is then started. After about 10 minutes the bubbles of gas will be found to practically disappear when passed into an azotometer which is filled with a 30% solution of potassium hydroxide. The carbon dioxide is then shut off and the oxidizing mixture added through the dropping funnel. As oxidizing fluid a mixture of 45% sulphuric acid and potassium dichromate is used in most cases. Just as effective as this solution however is a mixture of 40% sulphuric acid and potassium permanganate. In either case the mixture is added drop by drop to prevent too violent decompostion of the compound. After the mixture has been added the bulb of the decomposition flask is carefully heated to about 80° unless this temperature is reached spontaneously during the oxidation. Finally carbon dioxide is passed through the system again until the volume of nitrogen in the azotometer no longer increases. All other steps are similar to those employed in the regular Dumas nitrogen determination. The method is not applicable to substances that do

not give off the nitrogen readily. Heating to too high a temperature causes high results since gases that are not absorbed by potassium hydroxide are liberated on boiling the solution. If the substance is a liquid it must, of course, be sealed in a small bulb as in the Dumas method.

In the case of the hydrochloride of symmetrical diisopropyl-hydrazine, fairly close results are obtained on using Mohr's method in the halogen determinations. The primary isopropyl-hydrazine can not be used in the presence of potassium chromate since the latter is immediately reduced by the base.

DERIVATIVES OF SYMMETRICAL DIISOPROPYL-HYDRAZINE.- The neutral hydrochloride of this hydrazine is obtained as outlined in the isolation of the reduction products. The crude salt is recrystallized 3-4 times from very small amounts of alcohol to which ether may be added to complete the precipitation of the salt. Other recrystallizing agents that give good results are acetone and ethyl acetate. The salt is very soluble in water, and alcohol; insoluble in ether and in petrolic ether; and slightly soluble in all other common solvents. The hydrochloride is non-hygroscopic and has marked crystallizing properties, sometimes arranging in long hairlike needles that twine along the sides of the container for several inches. The substance melts at 198.5°(corr.) Conductivity determinations revealed the fact that, at high dilutions, the hydrochloride is appreciably hydrolyzed. Since the hydrazine is only as strong a base as hydrazine itself, this behavior of the hydrochloride is not unexpected.

Analyses: Calculated for $C_2H_{16}N_2 \cdot HCl$, N, 18.36; Cl, 23.27%

Found.- Cl,(Carius) 22.99;(Mohr's) 23.77;23.75;23.78;23.69%

N, (Dumas) 18.21% ; (Wet Method) , 18.15%

The remarkable results obtained with Mohr's method are interesting, since three different, independently standardized silver nitrate solutions were used and yet the results are all uniformly high in spite of the fact that the samples analyzed were also entirely different ones.

PHENYLTHIOSEMICARBAZIDE OF SYMMETRICAL DIISOPROPYL-HYDRAZINE.- This derivative is prepared by adding 1.25 mols of phenylmustard oil to 1 mol of the free hydrazine. To avoid overheating , the mixture is cooled until the reaction slows down. A good yield of a yellowish crystalline precipitate is obtained. The derivative is purified for analysis by recrystallization from absolute alcohol or from acetone. The corrected melting point of the pure substance is 129.4°. It is insoluble in water,but fairly soluble in the other common solvents.

Analyses.- Calculated for $C_{13}H_{16}N_3S$, N =16.74%; S = 12.75%.

Found; S, (Carius) 12.45; 12.45. N,(Dumas), 16.73%

BENZOYL DERIVATIVE.- A number of attempts to prepare the benzoyl derivative of the symmetrical hydrazine failed because the product was always a smear which could not be obtained in a satisfactory crystalline state. The Schotten-Bauman method and variations, as well as the Franzen method, using a benzene solution of the base instead of an alkaline solution is preparing the derivative, were tried during this work.

SEMICARBAZIDE OF SYMMETRICAL DIISOPROPYL-HYDRAZINE.- This

derivative is very readily prepared, difficult to purify for analysis. 1 mol of the hydrochloride of the base is dissolved in a little water to produce a saturated solution. To this mixture is added a mol of potassium cyanate. After a few minutes the mixture suddenly warms up to about 40° and a half crystalline half oily mass rises to the surface. On cooling the whole turns crystalline. Recrystallization, in turn, from hot alcohol, from ether and petrolic ether, from alcohol and petrolic ether, and from ethyl acetate, finally produces a product that melts at 100°(corr.). Further heating to as high as 225° produces no change in the melted substance. If not purified by the number of different recrystallizations described above, the melting point of the substance is unsharp usually beginning at 65° and finally melting at 85-90°.

Analyses.- Calculated for $C_7H_{17}N_3O$, N = 26.41%

Found, N = 26.26% and 26.18%.

OXALATE.- The oxalate is the most beautiful and the most easily prepared salt of the hydrazo compound, but, at the same time, the most difficult to obtain in the pure state. Free base, liberated as usual, is mixed with 10 volumes of dry ether and anhydrous oxalic acid added slowly until 1.2 mol of the acid has been added to two mols of the base. The whole mixture is a mass of snow white crystals as the precipitate forms immediately and is rather voluminous. Final purification is accomplished by six or more recrystallizations from alcohol followed by drying at 100° for 2 hours in a Storch drying tube evacuated by a good water pump. The salt thus purified and dried melts at 200° and appears to be perfectly pure, although the crude product is

composed of a mixture of substances that have very nearly the same properties.

Analysis.- Calculated for $C_8H_{34}N_4O_4$, N = 17.39%

Found .- Wet method. Sulphuric acid- potassium dichromate mixture, heated to boiling. N = 27.4% After 4 passages over hot copper oxide the apparent per cent of nitrogen decreased to 20%.

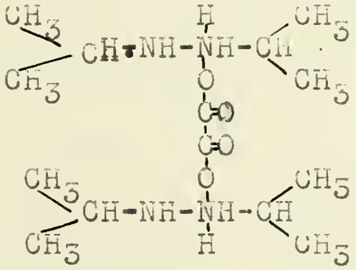
II Wet method, same oxidation method, but no external heating.

N = 17.43%

III. Same method. Same procedure.

N = 17.51%

The analyses show that the salt has the formula;



ACTION OF ALKYL HALIDES.- Among derivatives that were made only as test tube trials is the methyl iodide derivative. On heating a mixture of methyl iodide and the free dry base slightly the two react, with considerable evolution of heat, to form a mass of white crystals. The composition of this derivatives has not been studied. It is very soluble in water and in alcohol.

Isopropyl iodide or bromide refuse to react with the free base under all conditions tried. Even when a mixture of i-propyl alcohol, dry base, and isopropyl bromide are heated, in a closed tube to 110° for three hours no sign of a reaction product can be detected.

MONO-NITROSO DERIVATIVE OF SYMMETRICAL DIISOPROPYL HYDRAZINE.-

Early in the work with the hydrazo compound the reaction of nitrous acid on the base was shown to produce a straw colored light oil, that was obtained in variable yield under the conditions then selected. The product decomposed within a few hours and the compound was left for future study.

When the study of the derivative was taken up systematically two methods of preparation were developed.

First Method .- Twenty grams of the hydrochloride of the symmetrical hydrazine are dissolved in the least amount of water that will just dissolve the salt at room temperature. To this solution, 15 c.c. of alcohol are added and the resulting mixture cooled by a freezing mixture and vigorously stirred by a motor stirrer. When thoroughly cold a saturated aqueous solution of 25 g of sodium nitrite is added, and then, drop by drop, 15 c.c. of glacial acetic acid.

A thick layer of oil separates out as the reaction proceeds. When all of the acetic acid has been added the supernatant layer of yellow oil is separated from the lower layer. The mixture of salts and water is then extracted repeatedly with ether and the ether solution added to the separated oil. The final volume of the ether mixture should not exceed 100 c.c. This solution contains , as the most troublesome impurity a considerable amount of acetic acid. To remove the acid a few cc of water are added to the ether extract and the acid neutralized by means of sodium carbonate. After again separating the nitroso compound from the lower layer, the former is now dried for about 15 minutes with lumps of fused calcium chloride.

At the end of 1[illegible] minutes the calcium chloride is replaced by fresh lumps which are allowed to stay in contact with the ether extract for 1-2 hours. The liquid is then poured off and is ready for the final drying.

Second Method.- The second method of preparing the nitroso derivative consists in thoroughly mixing molecular amounts of dry sodium nitrite and dry hydrochloride of the hydrazo compound. To the well mixed powder, water is added until a thin paste is formed. This paste is then warmed in a water bath to 70 degrees and kept at that temperature for 1-1.5 hours. Although there is no noticeable reaction between the nitrite and the hydrochloride at room temperature, the reaction proceeds smootly at 70°. If the temperature is raised to 80-90° the product is discolored and the yield materially decreased due to decomposition. In the case of the product obtained by the first method heating to as much as 40° during the period when gas is liberated in the solution the whole lot of the product suddenly decomposes with evolution of heat and white fumes. This behavior has not been observed in case of the more stable product obtained by the second method. The layer of yellow oil is separated and the lower layer extracted with ether as in case of the first method. The ether solution is not dried with calcium chloride however, but is cooled in a freezing mixture to remove as much of the unchanged hydrochloride as possible. This is the main impurity obtained by the second method, and is readily removed on distillation. The yield is not quite as good (60-65% instead of 60-70% in case of first method) as that obtained by the first method.

The treatment of the nitroso derivative obtained by the two methods is identical after the calcium chloride treatment of the product obtained by the first method and the removal of the unchanged hydrochloride found in the product of the second method. The ether extract is dried over night over anhydrous sodium sulphate and kept cool, in the meantime, in an ice box. The decomposition of the small amount of di-nitroso compound that seems to be formed by the first method should be complete by next morning. The ice cooling is then discontinued, but the extract left in contact with the sodium sulphate for 3-4 days longer. When the liquid is then carefully poured off the sodium sulphate and distilled in vacuum the ether is readily removed without external heating, although time is saved by heating the solution to 25° by a water bath during this part of the distillation. As soon as all of the ether is removed, the yellow residual oil is distilled under a higher vacuum. At 6-8 mm the main protion of the liquid distills over between 64° and 66°. On redistiallation about 95% of the oil comes over between 65 and 66° at 7-8 mm pressure.

This pure product has a deep straw color, a peculiar sweetish odor, and is now stable at room temperature. Attempts to distill the oil at atmospheric pressure showed that this is impracticable since decomposition starts at about 150° and at the apparent boiling point of 160-2° the nitroso compound decomposes rather rapidly with evolution of white fumes. The yield of crude product could not well be determined and that of the pure oil is variable since the losses during drying and distillation are variable. On normal runs the yield of pure

nitroso derivative ranged from 50 to an occasional 70% of the calculated yield. The product is fairly soluble in water, slightly soluble in benzene and in petrolic ether, and readily soluble in alcohol, ethyl acetate, and ether. The derivative gives the Lieberman reaction, and shows other properties of nitroso compounds. If a drop of ferric chloride is added to an aqueous solution of a few drops of the derivative a blue-violet color is produced, in case of an alcoholic solution ferric chloride produces a green color, while a solution in chloroform(or even the dilute solution in benzene) shows a red coloration.

Analyses: Calculated for $C_6H_{15}N_3O$, N = 28.96%;C= 49.65;H=10.35%

Found; C , 49.65, 49.39%; H, 10.43, 10.22%; N, 28.66, 28.20%

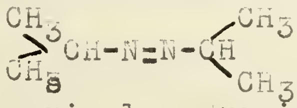
η_D^{23} = 1.4420 D 22/4 = .9440

SODIUM SALT OF THE NITROSO HYDRAZINE.- If the nitroso compound made. preferably, by the second method is diluted with ether and then treated with a saturated solution of sodium hydroxide in alcohol, the whole solution turns to a mass of very fine crystals after standing for a few hours. The same result is obtained when sodium methylate or ethylate is used instead of the saturated alcoholic solution of the hydroxide. The mass of needles is filtered off by suction, washed with ether and dried for 2-3 hours in a vacuum dessicator before the analysis is attempted. Since no solvent was found from which the salt could be recrystallized, the analytical results are only approximate, but sufficiently close to leave no doubt as to the compound obtained.

Analyses: Calculated for $C_6H_{14}N_3ONa$, Na = 13.77%; N,= 25.15%
Found: Na = 13.99% ; 14.54% ; N = 23.97%
The sodium was determined as the sulphate.

A peculiar reaction that was always observed when the nitroso derivative was heated in the presence of alkali or when it stood in contact with the alkali for longer periods of time, is the formation of a small amount of an isonitrile. An effort was made to isolate this product, but the yield is too small to isolate or detect the carbylamine except by its odor. It would thus be impracticable to prepare enough of the nitroso compound to be able to identify the isonitrile obtained from it.

A number of attempts were made to reduce the nitroso compound to the corresponding amine, but, as is usually the case when this type of nitroso compound is reduced, the only reduction products that could be isolated were ammonia and the original hydrazo compound. Attempts to affect the reduction by means of catalysis failed, apparently because the platinum catalyst is immediately poisoned by traces of free nitrous acid present. It was hoped that reduction of the sodium salt by means of the catalytic method would be a success, but only 4-5% of the theoretical amount of hydrogen gas was abosrbed.

2.2'-Azobispropane,  $(CH_3)_2CH-N=N-CH(CH_3)_2$.- Twenty grams of dry hydrochloride of the symmetrical hydrazine are treated with a 50% excess of dry powdered copper oxide. The substances are then thoroughly mixed by shaking the flask in which the reaction is allowed to take place. After about 15 minutes a peculiar sweet-

ish odor becomes noticeable, after an hour or two a trace of moisture may be noticed on some of the crystals, next morning the whole mass is distinctly moist and the odor of the oxidation product is much more marked. After 2-3 days the mass is so wet that it may be poured out of the reaction flask as a thick paste. After several days more, the reaction may be considered complete and the flask is connected to a condenser and heated gradually in a water bath. If the temperature is raised gradually, the large cubical ruby red crystals of an unstable copper salt, observed on the walls of the flask within 36 hours after the oxidation mixture was made up, suddenly change from red to greenish white while, at the same time, at 88.5°, the oxidation product begins to distil over as light, straw colored oil with a nauseatingly sweet and very characteriztic odor -- an odor that may be used as a very sensitive test for the hydrazo compound or its hydrochloride. The fraction distilling over between 92 and 98° is composed largely of water which forms a separate layer at the bottom of the reciever. The oil is readily separated from the water layer, the latter then extracted several times with ether, and the mixture of ether extract and oily layer dried for 24 hours over fresh fused calcium chloride. On redistillation the product almost all distills over between 88 and 89° as a mobile liquid with a faint straw color. The fact that the same intensity of color is obtained with every sample, shows that the color is not due to some trace of impurity. The corrected boiling point at 750 mm is 88.5° at which temperature over 90% of the oil distills over.

The pure oxidation product is neutral to litmus, is insoluble in acids and bases, and miscible with all of the common organic solvents. No derivative could be obtained with aqueous hydrocyanic acid, with potassium cyanate, with bromine, and with other reagents that often add on to double bonds.

The product in a 10 dm tube showed no absorbtion bands in the visible part of the spectrum when examined with a good spectroscope. At the extreme violet end of the visible spectrum a slight absorbtion seemed to occur, but no attempt was made to determine whether there is absorbtion in the ultraviolet or not, since suitable apparatus was not available at the time.

The index of refraction for sodium light when an Abbe refractometer was used was $\eta_D^{23} = 1.3890$. On a number of other samples of the pure product this value was obtained so that it is the most accurate value determined on any of the compounds. $D^{23}/4 = .7408$ as determined by means of a modified Sprengel picnometer.

The yield of oxidation product from 20 g of the pure hydrochloride is 21 cc of the moist and 19 cc of the pure oil. The calculated yield is 20 cc so that the yield obtained is practically quantitative.

The oxidation product is best prepared by the method described, but there are a number of other methods available for the preparation. As indicated previously, iodine titration goes quantitatively to the azo compound. Oxidation by means of any weak oxidizing agent produces the azo compound although the yield may be poor. Even such powerful oxidizing agents as

potassium permanganate and potassium dichromate produce a small amount of azo compound, as shown by the odor. In case a small amount of the oxidation product is needed on short notice it may be prepared with a yield of 60 to 70% by oxidizing the base by means of an alkaline copper salt solution. Copper acetate appears to give the best result. The hydrochloride and copper acetate are placed in a distilling flask. A dilute solution of sodium hydroxide is then added and the contents of the flask heated on a steam bath. The azo compound distills over as in case of the copper oxide-oxdiation experiments and ~~the azo derivative~~ is purified as in case of the regular method.

Analyses; Calculated for $C_6H_{14}N_2$; C = 63.15%; H = 12.28%; N=24.56%
Found ; C = 63.18%; 63.38%; 63.02%: H = 12.03 ; 12.45; 12.46%
N = 24.67%

Molecular Weight Determinations; (Freezing point lowering, Benzene)
Calculated = 114 ; Found 110 and 119.

Reduction of the Azo Derivative: Two cubic centimeters of azo compound reduced in a small reduction apparatus, absorbed the calculated amount of hydrogen in less than an hour under the influence of colloidal platinum as catalyst. Reduction with sodium amalgam or with sodium in alcohol yields the same product, the symmetrical diisopropyl hydrazine.

Hydrolysis of the Azo Compound .- The azo compound does not change to any appreciable extent after refluxing for an hour with a 2% solution of hydrochloric acid. After 4 hour of refluxing with a 4 % solution of the same acid no change could be noted, after 4 hours of refluxing with a 10% solution of the acid there was a considerable decrease in volume of the floating layer of azo

compound, but, at the same rate of hydrolysis at least 8 hours more would have been required to complete the hydrolysis. After one hour of treatment with a 20% solution of concentrated acid in water, the oily layer had practically all be used up. The compound is now hydrolyzed by refluxing with a mixture of 1 part of concentrated hydrochloric acid and 1 part of water. With this concentrated solution the layer of oil disappears within half an hour of refluxing. An extra half hour is usually used to be sure that the hydrolysis is complete. The mixture is then concentrated in vacuum until the resulting syrup becomes slightly colored. The hydrochloride of primary isopropyl hydrazine crystallizes out as small white needles on cooling the syrup in a freezing mixture. The salt is filtered off rapidly and the filtrate concentrated further until again syrupy. The freezing out and concentration processes are repeated until only a very small amount of residual solution is left. The small amount of hydrochloride left in this is precipitated by means of a mixture of a few drops of alcohol and about 5 c.c. of ether. The hydrochloride may then be purified and analyzed or the base may be liberated from the salt and the dibenzoyl derivative made in identifying this hydrolysis product.

To identify acetone - the other hydrolysis product- a second lot of azo derivative is hydrolyzed by a 10 % solution of hydrochloric acid. This does not cause as much loss of acetone as the more concentrated solution of acid does. After the hydrolysis is complete, the acetone is simply distilled off and identified by means of the benzilidine compound, by the iodoform test,

and by the sodium nitroprusside color test.

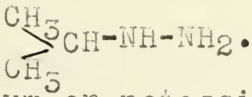
Conversion to the Hydrazone.- If the azo compound stands for a week or more over strong alkali or if it is heated for a few hours at 180° with concentrated potassium hydroxide, in a closed tube, the azo derivative is partially converted to the hydrazone as evidenced by the hydrazone odor, the greatly changed index of refraction, and the boiling point of 100° to 118° for the residue left on distilling off the unchanged azo compound. Since only a small amount could be obtained in a run of this kind the hydrazone could not be analyzed because the purification of such a small amount of product is too difficult. The fact that even such drastic treatment as heating to 180° only partially converts the azo to the hydrazone derivative shows that the azo derivative of symmetrical diisopropyl hydrazine is an uncommonly stable compound. All attempts to effect the reverse rearrangement - hydrazone to azo- failed.

Preparation of Di-isopropyl.- In tetra substituted hydrazines and in a few symmetrical disubstituted hydrazines oxidation or heat tend to decompose the azo compounds to produce nitrogen gas along with the dialkyl compound produced through reuniting of the two alkyl rests. In spite of a large number of different experiments carried out in an attempt to find a practical method of decomposing the azo compound obtained in this work into nitrogen gas and di-isopropyl, none of the methods tried gave more than traces of paraffins.

PREPARATION OF MONO ISO-PROPYLHYDRAZINE.- The primary hydrazine may be prepared by three different methods. Two of these, the hydrolysis of the azo derivative and of the hydrazone are similar and have been partly described. The hydrolysis of the hydrazone id effected by very dilute acids, even water hydrolyzes this compound, so the preparation of the primary hydrazine from this compound is extremely simple. Whether produced by hydrolysis of the hydrazone or of 2,2'-azobispropane the hydrolysis mixture is concentrated in vacuo as described before, the hydrochloride is isolated,and purified by recrystallization,and then decomposed by means of concentrated alkali.

The third and best method of preparing the primary hydrazine consists in the catalytic reduction of a mixture of 1 mol of pure acetone,1 mol of hydrazine hydrate, and 1 mol of hydrochloric acid in exactly the same manner that the reduction of ketazine was effected. The procedure throughout is the same except that the hydrochloride of primary isopropyl hydrazine decomposes too easily to permit the evaporation to dryness of the reduction mixture even in vacuo. Accordingly the hydrochloride is isolated by cooling the syrupy solution of the hydrochloride in a freezing mixture to freeze out as much as possible of the salt at a time. The mass of fine needle-like crystals is then filtered by suction. The filtrate is concentrated further and the freezing and filtering repeated until the amount of syrup left does not exceed 5 to 8 cc when the rest of the salt is precipitated by means of a little alcohol and a large excess of ether. By whatever one of the three methods mentioned, the salt may have been

obtained, the isolation of the hydrochloride is accomplished in exactly the same manner. The hydrochloride obtained through hydrolysis of 2,2'-azobispropane by 50:50 hydrochloric acid is very hygroscopic, while those obtained from the hydrazone and from the reduction of the acetone-hydrazinehydrate mixture are only very slightly hygroscopic. The hygroscopic salt was not analyzed, but since the non-hygroscopic salt proves, through analyses, to be the neutral salt, there is little doubt about the identity of the hygroscopic compound, especially since both hydrochlorides yield the same base on treatment with concentrated alkali, so that one must be the acid and the other the neutral salt unless they be the same compound. This is not the case, however, since recrystallization does not yield a non-hygroscopic salt melting at 114.5°.



ISOLATION OF PRIMARY ISOPROPYLHYDRAZINE, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\text{-}NH\text{-}NH_2$.- On treatment of the hydrochloride with solid sodium or potassium hydroxide the mono isopropyl hydrazine is liberated as an oil that, in appearance and odor, is very similar to the symmetrical hydrazine described previously. The base cannot, however, be obtained in a pure state by any method or device tried so far. A constant of tiny bubbles, usually starting from some fine dust particle or sharp point, is ~~constantly~~ given off for an indefinite period of time. The amount of gas given off is so small that a very large amount of product or a very long period of time would be necessary to collect enough gas to identify it. As the oxidation of primary hydrazines results in the elimination of nitrogen, it is probable that the gas escaping is nitrogen gas.

The accurate determination of the density is made impossible by the gas evolution, and indeed would be of little value on a compound that is admittedly not pure. The index of refraction shows that the hydrazine gradually decomposes. The purest fresh base examined gave a boiling point of 106-7 at 748 mm and had a density of .814 at 25 degrees. $\eta_D^{23} = 1.4280$

The base is miscible with water, alcohol, acetone, and ethyl acetate, but only slightly soluble in ether and petrolic ether.

Primary isopropyl hydrazine is a very strong reducing agent, in this respect even excelling the symmetrical hydrazine. In addition to reducing silver nitrate solutions and Fehling's solution in the cold, it also reduces potassium chromate as was shown when an attempt was made to determine the chlorine of the hydrochloride by means of Mohr's method.

Iodine titrations and hydrochloric acid titrations may be used as in case of the symmetrical hydrazine.

In as much as the base is known to be impure, no attempt has been made to analyze it. To prove its identity conclusively the hydrochloride, the phenylthiosemicarbazide, and the dibenzoyl derivatives were prepared and analyzed.

DERIVATIVES OF PRIMARY ISOPROPYLHYDRAZINE.-

The hydrochloride has been partially described in connection with the hydrolysis of the azo and hydrazone derivatives (page 64-65) The crystals isolated from the residue left on concentration of the hydrolysis or the reduction mixture, are dissolved in a very small amount of alcohol. After heating to dissolve all of the crystals ether is added to the solution

until the first permanent cloudiness is obtained. On cooling this solution to -10°or lower by a good freezing mixture, the salt crystallizes out. The alcoholic filtrate should never be discarded,however, since the hydrochloride is so extremely soluble that, even at -10° much more stays in solution than is frozen out. Two such treatments give a product that is sufficiently pure to be analyzed. Ethyl acetate may be used as a recrystallizing agent but the hydrochloride is only very slightly soluble in ethyl acetate and large amounts of the solvent must be used to obtain a fair sized crop of crystals on freezing the solution.

The pure hydrochloride is non-hygroscopic(i.e. if we are working with the neutral salt) melts at 114.5° (corr.),and is very soluble in water and in alcohol, slightly soluble in chloroform,benzene,ethylacetate, and acetone, and insoluble in ether and petrolic ether.

Analyses; Calculated for $C_3H_{10}N_2HCl$, N = 25.34 %

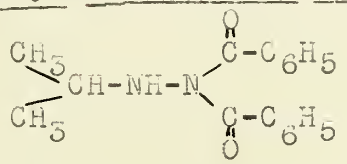
Found; N = 25.39%

Phenylthiosemicarbazide of Primary Isopropyl-Hydrazine.- When a mol of phenylmustard oil is added to an ether solution of 1 mol of free primary isopropylhydrazine, fine long needles of the mustard oil derivative precipitate out in a few minutes. These are recrystallized from alcohol by adding water or ice to a hot solution of the derivative in alcohol. When the first permanent cloudiness appears on adding water, the solution is cooled well when the derivative precipitates out in good yield. The melting point of the pure derivative is 141.5°(Corr.). It is very soluble in hot alcohol, in acetone, chloroform, and ethylaacetate, and insoluble in water, ether, and petrolic ether.

Analyses: Calculated for $C_{13}H_{15}N_3S$, N = 20.09%

Found. (Dumas) N = 19.86 and 20.23%.

Di-Benzoyl Derivative of Primary Isopropyl-Hydrazine,



.- Two mols of benzoyl chloride are added to a concentrated solution of the hydrochloride in water. Sodium carbonate, in excess is added to this. After a few minutes of lively stirring a reaction occurs with evolution of considerable heat. At first no precipitate or other product can be detected. After stirring and rubbing the smear with sodium carbonate a few minutes the derivative suddenly crystallizes out. Purification is accomplished with alcohol and water in exactly the same manner as in the case of the phenylthiosemicarbazide derivative. The pure product consists of beautiful white needles melting at 161.5°(corr.) The dibenzoyl derivative insoluble in water, ether, and petrolic ether, while it is soluble in alcohol, ethyl acetate, and benzene.

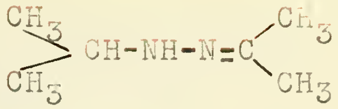
Analyses: Calculated for $C_{15}H_{18}N_2O_2$, N = 9.93%

Found: (Dumas) 9.85% and 10.09% N .

Even when only one mol of benzoyl chloride is added to 1 mol of the base the same derivative is formed while the remainder of the base is not affected.

Other Derivatives;Test tube trials show that the oxallate, the picrate, the semicarbazide, and the aromatic aldehyde derivatives can readily be prepared. To prepare the aliphatic aldehyde and ketone derivatives, a condensing agent appears to be necessary.

PREPARATION OF ACETONE ISOPROPYL-HYDRAZONE,



$(CH_3)_2>CH-NH-N=C<(CH_3)_2$.-

Although preliminary trials had shown that a small amount of a new compound was obtained when the primary hydrazine and acetone were mixed, the yield was too small to permit the isolation and identification of the new substance. As it was very urgently desired to make the condensation product of acetone and the primary hydrazine, to prove , if possible , the structure of the oxidation product obtained from the hydrochloride of the symmetrical hydrazine, a long series of experiments were carried out in an effort to determine whether the condensation product could be produced in good enough yield to permit,at least , its isolation and identification.

The only method that has been tried that gives good yields is the one developed by Reddelien[45] for the preparation of aniles. 1.5 mols of acetone of acetone are added to a solution of 1 mol of primary isopropyl hydrazine in 10 volumes of ether that has been carefully dried. No reaction can be noticed. A small piece of anhydrous zinc chloride (less that .5 g) is added to the mixture. Immediately there is a violent reaction with vigorous heating and ebulition of acetone. To prevent too large a loss of acetone the small flask is cooled under the tap until the reaction slows down. The mixture is again heated almost to the boiling point of the excess acetone and then allowed to stand for an hour or two. At the end of this time the reaction product is distilled directly off the liquid and cheesy zinc salts. The distillate is then dried over freshly dried anhydrous sodium sulphate for 3-4 days before fractionating the mixture. Up to

65° the ether and excess acetone come over. At about 65° the thermometer suddenly rises until a temperature of 132° is reached. The rest of the liquid distills over between 132 and 134 degrees. The residue left after this, as well as the first distillation is a **deep** red liquid containing zinc salts as some of the residual substances. These substances were not examined in detail.

The pure hydrazone is a colorless, mobile liquid with a stinging menthol odor that seems to be characteriztic of ketone and aldehyde condensation products with primary isopropyl-hydrazine, as it was also encountered in test tube experiments with benzaldehyde and with salicylaldehyde.

The density was found ; $D^{26.5/4} = .8225$

The refractive index ; $\eta^{22}_{D} = 1.4360$

Analyses: Calculated for $C_6H_{14}N_2$, $C = 63.15$; $H = 12.28$; $N = 24.56\%$

Found: $C = 62.69$ and 63.00%; $H = 12.47, 12.55\%$; $N = 24.98, 24.34\%$

Molecular weight determination. Lowering of freezing point of benzene. Found + 105,108, 104 . Theoretical : 114.

The hydrazone is very easily hydrolyzed even by water. This fact explains why it has been so difficult to obtain aliphatic hydrazones in the past. The products of hydrolysis were identified in the same way that those obtained from the azo compound were identified.

Reduction to the hydrazo compound was readily effected by means of colloidal platinum and hydrogen as in the case of the azo compound. The product obtained was identified by the melting point of the hydrochloride and by the odor of the azo compound

obtained on treating the hydrochloride with powdered copper oxide.

Attempts to prepare the benzoyl, the phenylmustard oil, and the semicarbazide derivatives failed because , owing to moisture perhaps, the final product obtained was always the corresponding derivative of the primary isopropyl hydrazine. It is possible that some of these may be obtained through the use of some dehydrating agent.

VARIOUS DETERMINATIONS AND METHODS:-

The index of refraction of the different compounds was determined by means of an Abbe refractometer with daylight as the source of light. The instrument was frequently checked against water. The temperature was obtained by means of a Normal thermometer.

The specific gravity was determined,in each case ,by means of a small modified Sprenkel type picnometer. Because of the small amounts of pure material prepared,in most cases,at one time, the capacity of the picnometer was made only 1.6219 cc at 4 degrees. The instrument was always filled to the mark on the fine capillary side arm at the temperature at which the sample and instrument had been kept for some hours. This temperature was known and was higher than that of the balance case. When the weighings were carried out the liquid drew away from the tip of the instrument thus preventing loss due to evaporation.

To determine the strength of the symmetrical hydrazine, and if possible, that of the primary hydrazine, conductivity measurements were carried out. The temperature of the thermostat was kept constant at 25 ± .01°. The cell had platinized

electrodes fastened, to a vertical double wire inlet tube, parallel to each other and at a distance of 2.5 mm. A stopcock at the bottom of the cell permitted the withdrawal of 5 cc of solution after each dilution while the added water was added from an accurately calibrated pipette. As the samples had to be kept in an atmosphere of nitrogen, a strong capillary tube reaching into the bottom of the cell served as an inlet for the nitrogen which served as a stirring device as well as in the capacity of an inert atmosphere. This proved very satisfactory as the bubbles stirred the solution thoroughly without endangering the adjustment of the electrodes.

The sourse of alternating current was a special alternator furnishing 1000 cycles a second. The conductivity water was prepared by means of the regular conductivity water still.

As the hydrochloride is appreciably hydrolyzed at high dilutions , Bredig's method of calculating the value of Λ_∞ was employed. No claim of great accuracy is made for the determinations in view of the fact that it is very difficult to prevent the base from oxidizing to some extent and the assumption that hydrolysis does not enter in in the conductivity determinations on the hydrochloride below 256 volumes is also hardly justifiable. In view of the limitations placed on the conductivity work by the nature of the base, the fact that the strength of the symmetrical base is very close to that of hydrazine, is all that was hoped for the determinations.

The primary hydrazine proved to be extensively hydrolyzed even at 16 volumes of water to 1 of base.

TABLE II.

Conductivity, at Various Concentrations, Of the Hydrochlorides Of Some Nitrogen Bases.

Volumes of Water per Gram of Salt.	Hydrochloride of				
	2,2'-Hydrazopropane	N_2H_4	$(CH_3)_2NH$	NH_3	CH_3NH_2
8	82.1	---	---	---	----
16	102.0	---	---	---	----
32	116.2	111.5	106.3	126.3	113.4
64	130.0	114.6	109.7	129.8	116.9
128	140.0	117.8	112.6	132.8	119.9
256	160.0	120.8	114.0	135.0	122.6
512	175.0	122.5	116.2	136.4	123.8
1024	182.0	125.0	117.5	137.9	125.1

Data, except for 2,2'-hydrazopropane(Symmetrical diisopropyl hydrazine), from Bredig.[52]

TABLE III

Values of $\frac{100\alpha^2}{(1-\alpha)v}$ for a Number of Nitrogen Bases at Various Concentrations.

Base	Volumes = 8	16	32	64	128	256	Average
Hydrazine	.00044	.0003	.00023	.00021	.00020	.00021	.00027
Sym.Di-iso Propyl-hydrazine	.00023	.00022	.00019	.00018	.00019	......	.00020
Aniline	.157	.163	.162	.159	.156	.152	.158
I-Propyl-amine	.052	.054	.054	.053	.052	.051	.053
Ammonia	.0023	.0023	.0023	.0023	.0023	.0024	.0023
Methyl-amine	.052	.052	.051	.050	.049	.047	.050
Dimethyl-amine	.074	.074	.074	.074	.074	.074	.074
Trimethyl-amine	.0069	.0073	.0075	.0076	.0075	.0074	.0074

Data, except for symmetrical diisopropyl-hydrazine, from Bredig(52)

IV SUMMARY.

1) The reduction of dimethyl ketazine to symmetrical diisopropyl hydrazine has been accomplished by means of catalytic reduction using colloidal platinum as a catalyst.

2) The resulting hydrazine and its common derivatives have been studied.

3) 2,2'-Azobispropane has been prepared by oxidation of the hydrochloride of the symmetrical hydrazine. The use of copper oxide as an oxidizing agent to prepare aliphatic azo compounds constitutes a new method of oxidation of such nitrogen compounds.

4) Acetone-isopropyl hydrazone , a new type of aliphatic compound has been prepared and studied. The isolation of both the azo and the hydrazone derivatives of the symmetrical hydrazine represents an achievement that has not heretofore been accomplished in the field of purely aliphatic hydrazines.

5) The mono-nitroso derivative of symmetrical diisopropylhydrazine has been prepared and studied.

6) The first sodium salt of a purely aliphatic nitroso-hydrazine has been prepared in the form of the sodium salt of the mono-nitroso derivative of the symmetrical hydrazine.

7) The previously unknown primary isopropyl hydrazine has been prepared by the following methods;

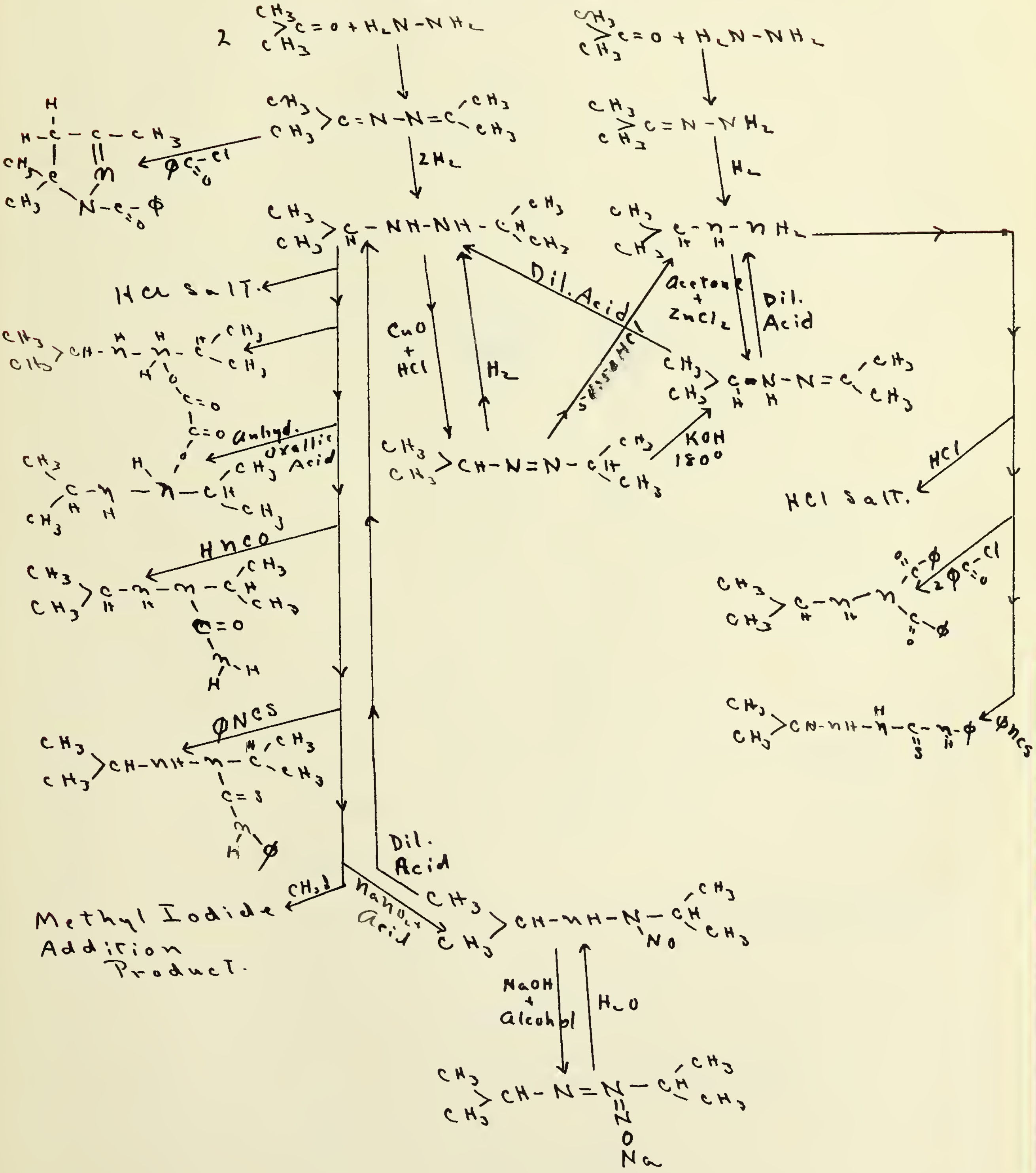
(a) By reduction of a mixture of 1 mol of acetone and 1 mol of hydrazine hydrate to which 1 mol of hydrochloric acid had been added.

(b) By acid hydrolysis of acetone isopropyl hydrazone.

(c) By acid hydrolysis of 2,2'-azobispropane.

TABLE IV

Relations Between the Different Products Studied in the Present Investigation.



BIBLIOGRAPHY.

1. Curtius, J.prakt.Chem.,(2) 38,531 (1888)

2. Raschig, Ber.40, 4587 (1907)

3. Fischer, Ann.,190,71 (1878)

4a. Fischer, Ann., 190, 77 (1878)

4b. Fischer, Ann., 199, 308(1879)

4c. Fischer, Ber., 13, 2171(1880)

5a. Fischer, Ann.,199,325 (1879)

5b. Fischer, Ann.,190,102 (1878)

6. Fischer and Brüning, Ann.,253, 5 (1889)

7a. Fischer, Ann.,199,330 (1879)

7b. Fischer, Ber.,29,793 (1896)

7c. Harries and Haga, Ber.,31, 58 (1898)

8. Stolle and Benrath, J.prakt.Chem.,(2) 70,263(1904)

9. Busch, Dissertation, Heidelberg, 1904.

10. Kischner, J. prakt.Chem.,(2) 64,113 (1901)

11a. Curtius, J. prakt.Chem.,(2) 39,44 (1889)

11b. Curtius and Pflug, J.prakt.Chem.,(2) 44,535 (1891)

12a. Curtius, J. prakt. Chem.(2) 62,83(1900)

12b. Thiele, Ann.376,261 (1910)

12c. Curtius,Propfe,and Haager,J.prakt.Chem.,(2)44,164(1891)

13a. Curtius,J.prakt.Chem.,(2) 62,83(1900)

13b.Wohl and Oesterlin, Ber.,33,2736(1900)

14.Curtius and Thun, J.prakt.Chem.,(2) 44,161(1891)

15, Thiele, Ann.,376,262 (1910)

16. Thiele and Heusser,Ann.,290,30(1896)

17.Wieland,"Die Hydrazine, Ferdinand Enke,Stuttgart,1913.p 94

18. Mailhe, Compt.rend.,170,1265 (1920)

18a. Curtius and Foersterling,Ber.27,770(1894)

18b. Curtius and Zinkeisen,J.prakt.Chem.,(2)58,310(1898)

18c.Franke, Monatsh.,20,855(1899)

18d. Frey and Hoffman, Monatsh.,22,762(1901)

19. Curtius and Wirsing, J.prakt.Chem.(2) 50,546(1894)

20.Ziehl, Dissertation, Göttingen,1914.

21. Staudinger, Helv.Chim.Acta, 4,212,217,239(1921)

22a. Kauffman, Ber.51,123 (1918)

22b.Willstätter, Ber.,51,767(1918)

22c.Rosenmund,Ber.,51,580(1918)

22d. Willstätter,and Mayer, Ber.,41,1475(1908)

23a. Loew, Ber.,23,289(1890)

23b. Willstätter,and Hatt, Ber.,45,1471(1912)

24a. Paal and Amberger, Ber.,37,124(1904)

24b. Paal, Ber.45,2221(1912)

24c.Borsche,Ber.,52,2077(1919)

25a. Skita and Meyer, Ber.,45,3513,3579,3589(1912)

25b. Rabe,Ber.,45,2166(1912)

25c. Skita, Ber.,42,1627(1909)

25d. Skita, Ber.,52,1520(1919)

27a. Harries, Ber.,27,2279(1894)

27b.Harries and Klamt, Ber.28,504(1895)

27c. Knorr and Köhler,Ber.,39,3259(1906)

27d.Thiele, Ber.,42,2577(1909)

27e. Harries and Haga,Ber.31,62(1898)

28a. Korte, Dissertation, Heidelberg,1903.

28b. Busch, Ber.,36,139(1903)

29a. Dr.J.R.Bailey, Private Communication.

29b. Harries and Haga, Ber., 31,64(1898)

29c. Harries, Ber.27,2276(1894)

30a. Thiele, Ber.,41,2806(1908)

30b. Thiele, Ber.,41,2681 (1908)

30c. Stolle, Ber., 41,2811(1908)

31. Curtius, Ber.,33,2562(1900)

32.Bamberger and Hausser, Ann.,375,319(1910)

33a. Voswinkel, Ber.,35,1943(1910)

34.. Pechman, Ber.26,1047(1893)

35. Bamberger, Ber.,35,758(1902)

36.Thiele , Ann.,376,243 (1910)

37. Kizis, Dissertation, Strassburg, (Date not given)

39. Wieland, loc.cit.page 44.

40. Baeyer, Ber.,2,683(1869)

41a. Gomberg, Ann.,300,60(1898)

41b. Schmittman, Dissertation, Heidelberg,1914).

41c.Thiele and Heusser, Ann., 290, 261(1896)

42. Mitcherlich, Ann.12,311(1834)

43a. Fischer, Ber.,29,793(1896)

43b.Bamberger and Pemsel,Ber., 36,56(1903)

43c.Elbers, Ann.,227, 354(1885)

43d. Thiele, Ann.376,267(1910)

44a. Thiele and Heusser,Ann.,290,6(1896)

44b.Hantsch and Lifschütz , Ber.,45,3016(1912)

45a. Elbers, Ann., 227,354(1885)

45b. Thiele,Ann.,376,267(1910)

45c. Kischner,J.prakt.Chem.,52,424 (1895)

45d. Kischner,J.prakt,Chem.,(2)64,125(1901)

46a. Reddelien, Ber.42,4759(1909)

46b. Reddelien, Ber.,43,2479(1910)

46c.Reddelien, Ann.,388,170(1912)

46d. Lachowiez,Monatsh.,9,510(1912)

46e. Reddelien, Dissertation ,Leipzig(1912)

47. Dimroth and Zoeppritz, Ber.,35,984(1902)

48. Wieland, Ber.,41,3506(1902)

49.Shipley and Werner, J.Chem. Soc.,103,1255(1898)

50. Stolle, J.prakt.Chem.,(2) 66,332(1902)

51. Storch, Centralbl.1893,I,915.

52. Bredig, J.prakt.Chem. 13,308(1891)

53. Noyes, J.A.C.S.,43,1779(1921)

BIOGRAPHY.

The writer was born in Gillespie County, Texas, on October 18th, 1892. He graduated from the Southwest Texas Normal School in 1913, with History as the major study. In 1918 he recieved a B.A. degree from the University of Texas where he served as student assistant in 1917-18, and as tutor in 1919-20. Previous to and between his years of study at the University of Texas, he taught for four years in various public schools of Texas.

From April 1918 to September 1919, he served in the hospital corps of the U.S.Navy, in clinical laboratory work.

He was a graduate assistant in Chemistry during 1920-21 and a Fellow during 1921-22 at the University of Illinois.

He is co-author of two articles.-

1) "The Conversion of Methyleneaminoacetonitrile to Iminiacetonitrile" by J.R.Bailey and H.L.Lochte, J.A.C.S. 39,2443 (1917)

2) "Symmetrical Di-Isopropyl-Hydrazine and Its Derivatives." A preliminary article by the writer with J.R.Bailey and W.A.Noyes. J.A.C.S. 43,2597 (1921)